CESEP'19 CONFERENCE

8th International Conference on Carbon for Energy Storage and Environment Protection

October 20 - 24th

Alicante (Spain)

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Welcome to CESEP ´19

The 8th Internacional Conference on

Carbon for Energy Storage and Environment Protection

CESEP'19 is the eighth international conference on Carbon for Energy Storage and Environment Protection. The conference is organized by the Spanish Group of Carbon (GEC) and will be held in Alicante, Spain.

Carbon materials play a major role in a large number of highly specialized applications -as structural and functional materials- related with current industrial challenges. The underlying reasons for this are their flexible coordination chemistry that allows almost infinite possibilities of structures, and their ability to react with other heteroatoms to incorporate functional groups that determine the self-organization, chemical stability and reactivity.

Topical areas include structural and nanotextural characterization, gas separation and gas storage, solar energy conversion, carbon as catalyst and catalyst support, adsorption of gas-phase pollutants, carbon in green chemistry and recycling processes, carbon for water production and remediation, supercapacitors, lithium batteries and other advanced batteries, fuel cells, biological and health applications of carbons, carbon materials in sensor and biosensor, in-situ and operando studies, simulation and computational methods, demonstration systems.

This conference is expected to stimulate fruitful discussion, new ideas and collaborations between specialists from various domains. As in preceding meetings, the conference aims at bringing together the scientists, engineers and technologists and intends to provide a forum for discussion on fundamental and technological scientific aspects of carbon applications related to energy storage and environment protection.

In keeping the style of the first CESEP, the Conference will consist of one single session (no parallel sessions!) and will comprise 2 invited plenary lectures, 11 keynotes and selected contributions of oral and poster communications. About 140 communications have been received and the publication of a special issue in Journal of Carbon Research (MDPI) has been scheduled.

We would like specially to thank the following institutions and companies for their financial support: University of Alicante, Catienza (Aplicaciones y Procesos de Vacío), InProcess Instruments, Netzsch, Iberfluid and Metrohm.

I would like to acknowledge and appreciate the work performed by all members of the participating committees, specially the local committee.

We hope you will enjoy the meeting and that you will have time to interact one to another and to visit our host city. Alicante is a seaside, cozy and sunny city, with an excellent weather and a nice atmosphere.

Mª Jesús Lázaro
Conference Chair

ORGANIZERS

Grupo Español del Carbón (GEC)

Universidad de Alicante (UA)

Instituto Universitario de Materiales de Alicante (IUMA)

AWARDS AND SPONSORS

The Spanish Carbon Group and Process Integral Development Eng&Tech, S.L. (A Micromeritics Company) will sponsor two awards for the best oral presentations. Each award will comprise 100 Euros and a presentation certificate.

The Royal Society of Chemistry will sponsor two awards for the best poster presentations offered by the journals Energy & Environmental Science and Sustainable Energy & Fuels. Each award will comprise a 50 GBP RSC Books voucher and a presentation certificate.

CONFERENCE COMMITTEES

Executive Committee

- María Jesús Lázaro-Elorri (President of the Spanish Carbon Group)
- Francisco Carrasco-Marín
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- Manuel Sánchez-Polo
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- María Olga Guerrero-Pérez
- Miguel Ángel Gilarranz-Redondo
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- David Salinas-Torres
- Joaquín Silvestre-Albero
- Miriam Navlani-García

ADVISORY BOARD

PLENARY SPEAKERS

"Metal-free porous carbon catalysts for ORR: Addressing the complexity of activity governing factors"

TERESA J. BANDOSZ, Ph.D., D.Sc.

City College of New York, U.S.A.
Dr. Bandosz has Ph.D. In Chemical Engineering and D.Sci. in Physical Chemistry.

She is a full professor of Chemistry and Chemical Engineering at the City College of New York. For three years she was associated with Dalian University of Technology in China as a sky scholar/ guest professor of Chemical Engineering.
Dr. Bandosz is a Fulbright Senior Scholar (2016/2017). She edited the book "Activated carbon surface in environmental remediation," published by Elsevier (2006).
Her work during last 30 years has resulted in 6 US patents and over 400 publications in peer-reviewed journals (H index 59 (excluding self-citations)).
Her recent research interests include synthesis of graphene-based composites for separation and energy harvesting applications, visible light photoactivity of carbonaceous materials, energy storage, ORR and CO_2 sequestration and reduction. Since 2014 she is coeditor of Journal of Colloid and Interface Science. She served on the Advisory Board of American Carbon Society. She is on the Board of Directors of International Adsorption Society and on the Editorial Boards of Carbon, C, Adsorption Science and Technology, Chemical Engineering Journal and Applied Surface Science.

"A Challenge Using Classic Carbon Materials to Progress of Electrochemical Capacitors"

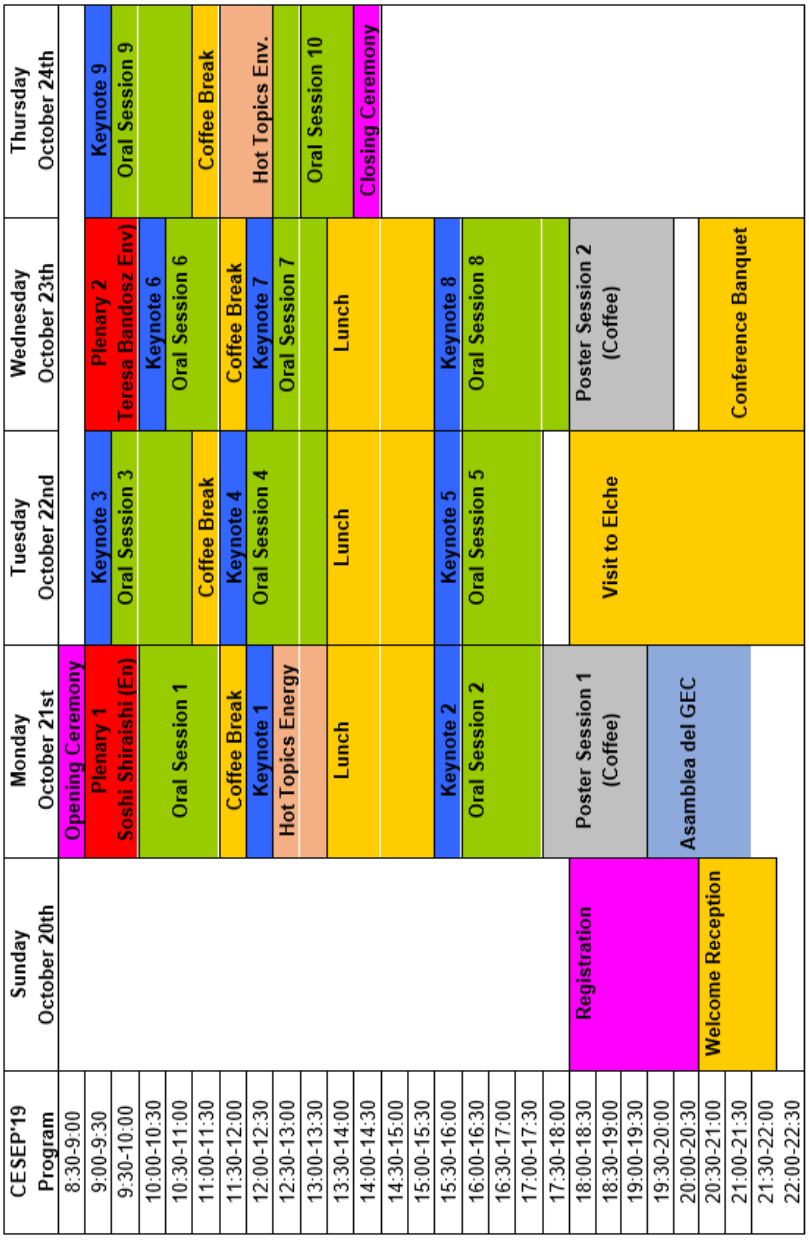
SOSHI SHIRAISHI, Ph.D.
University of Gunma, Japan.

Prof. Soshi Shiraishi received his PhD degree in 1999 from Kyoto University under the supervision of Prof. Y. Ito.
In 1997 he became an assistant professor at the University of Gunma, where he now works as full professor. He also acted as chief editor of the Carbon Society of Japan in 2012 and 2013.
He has received numerous awards such as the Young researcher award of the Carbon Society of Japan (2004), the Young researcher award of the Electrochemical Society of Japan (2006), the Japan Carbon Award for Young Researcher (2008), and the Carbon Society of Japan Award (2014). His main research interests are related to the development and use of porous carbon materials in energy storage

TOPICAL AREAS

- Synthesis of new forms of carbons and surface functionalization by different methodologies
- Structural and nanotextural characterization
- Gas separation and gas storage
- Solar energy conversion
- Carbon as catalyst and catalyst support
- Adsorption of gas-phase pollutants
- Carbon in green chemistry and recycling processes
- Carbon for water production and remediation
- Supercapacitors
- Lithium batteries and other advanced batteries
- Fuel cells
- Biological and health applications of carbons
- Carbon materials in sensor and biosensor
- In-situ and operando studies
- Simulation and computational methods
- Demonstration systems

SCIENTIFIC PROGRAM
TIME SCHEDULE



DAILY SCIENTIFIC PROGRAM

Monday, October 21st

(8:30-9:00) OPENING CEREMONY

(9:00-10:00) PLENARY LECTURE 1

A Challenge Using Classic Carbon Materials to Progress of Electrochemical Capacitors
S. Shiraishi

(10:00-11:30) ORAL SESSION 1

S1-1
A green strategy towards high-surface area carbons by chemical activation of biomass-based products with sodium thiosulfate
Antonio B. Fuertes, Guillermo A. Ferrero, Noel Diez, ***Marta Sevilla***

S1-2
Low-cost biochar produced by hydrothermal carbonization of compost derived from municipal Solid Waste
F.F. Roman*, J.L. Diaz de Tuesta, A.M.T. Silva, J.L. Faria, P. Praça, H.T. Gomes*

S1-3
Recovery of graphitizable structure in activated carbons after the KOH activation process
Navarro P., Collados C., Romero-Anaya A., Silvestre Albero, J., ***Martínez Escandell, M.***

S1-4
Synthesis of ordered mesoporous carbons by a photoinduced strategy
Maria C. Fernandez de Cordoba*, Lavinia Balan, Conchi O. Ania*

S1-5
Development of novel PAN-based activated carbon fibers
Masaaki Yoshikawa*, Junichi Hayashi*

S1-6
Biomimetic calcium-deficient hydroxyapatite deposited on carbon fiber cloth for bone regeneration
Olivier, F., Delpeux, S., Chancolon, J., Warmont, F., Sarou-Kanian, V., Fayon, F., Rochet, N., ***Bonnamy, S.***

(11:30-12:00) COFFEE BREAK

(12:00-12:30) KEYNOTE 1
Force-driven reversible liquid–gas phase transition mediated by elastic nanoporous carbon materials
Hirotomo Nishihara*, Keita Nomura, Masanori Yamamoto, Masashi Ito, Masanobu Uchimura, Hideki Tanaka, Minoru T. Miyahara & Takashi Kyotani*

(12:30-13:30) HOT TOPICS ENERGY

HT1
How next generations of electrochemical capacitors can be developed with help of carbon porosity?
Patryk Przygocki, Emmanuel Pameté-Yambou, Barbara Gorska, ***François Béguin***

HT2
Ageing of carbon based electrochemical capacitors in neutral aqueous electrolyte
Elzbieta Frackowiak, *Justyna Piwek, Anetta Platek, Krzysztof Fic*

HT3
Electron conducting cement/carbon nano-composites: expanding concrete structural elements functionalities
Nicolas Chanut, *Katerina Ioannidou, Thibaut Divoux, Rénal Backov, Franz-Josef Ulm and Roland J.-M. Pellenq*

HT4
An asymmetric supercapacitor-diode (CAPode) for unidirectional energy storage
Natalia Fulik, *En Zhang, Guang-Ping Hao, Han-Yue Zhang, Katsumi Kaneko, Lars Borchardt, Eike Brunner, Stefan Kaskel*

(13:30-15:30) LUNCH

(15:30-16:00) KEYNOTE 2
Optimizing porous carbons for supercapacitors operating in high concentrated aqueous electrolytes
C. Neto, M. Deschamps, ***E. Raymundo-Piñero***

(16:00-17:15) ORAL SESSION 2

S2-1
Capacitance vs. current density in microporous carbon monoliths
José M. Rojo*, Iván Aldama, María Angeles Lillo-Ródenas, Mirko Kunowsky, Javier Toro, Joaquín Ibáñez*

S2-2
Carbon monoliths with an ordered mesoporous structure from coal tar-derived products for electrochemical energy storage
A. Castro-Muñiz, *S. Lorenzo-Fierro, A. Martínez-Alonso, J.M.D. Tascón, F. Suárez-García, J. I. Paredes*

S2-3
Utilization of whey for the synthesis of nitrogen doped carbon xerogel supercapacitors
L.A. Ramírez-Montoya*, S. Fernández-Villanueva, Raúl Llamas-Unzueta, A. Arenillas, M.A. Montes-Morán, J.A. Menéndez*

S2-4
Cellulose-based activated carbon fibers for use as supercapacitor electrodes
***Breitenbach Stefan**, Unterweger Christophol, Fürst Christian, Hassel Achim Walter*

(17:30-19:30) POSTER SESSION 1/ COFFEE
All poster communications will be presented in both Poster Session 1 and 2, and should be on display from Monday morning, October 21st, until the end of Poster Session 2, Wednesday. October 23rd, 20:00h. Titles and authors of the poster communications are shown at the end of the conference program.

Tuesday, October 22nd

(9:00-9:30) KEYNOTE 3
Efficient cathodic exfoliation of graphite in aqueous electrolytes towards high quality graphene for energy and environmental applications
***Sergio García-Dalí**, Juan Ignacio Paredes, José María Munuera, Silvia Villar-Rodil, Amelia Martínez-Alonso, Juan Manuel Díez Tascón*

(9:30-11:00) ORAL SESSION 3

S3-1
Fe-N-doped hydrothermal carbons for the oxygen reduction reaction
***N. Rey-Raap**, R. G. Morais, J. L. Figueiredo, M. F. R. Pereira*

S3-2
Porous activated binderless pellets for electrochemical oxygen reduction and evolution reaction
***Guillermo A. Ferrero**, Feihong Song, Anna Mechler, Robert Schlögl, and Saskia Heumann*

S3-3
Synthesis of N-doped graphenic foam for the oxygen reduction reaction in PEMFC
*Lilian Moumaneix, **Sébastien Fontana**, Sébastien Cahen, François Lapicque, Claire Hérold*

S3-4
Recycling the spent bleaching earth waste material into electrocatalytic component
*D. Fernández-Inchusta, B. Aghabarari, M.J. Lázaro, **M.V. Martínez-Huerta***

S3-5
How to make a proper 3D characterization of PEMFC catalyst layer?
***Fabien L. Deschamps**, Julien G. Mahy, Alexandre F. Léonard, Stéphanie D. Lambert, Adrien Dewandre, Benoît Scheid, Nathalie Job*

S3-6
Graphitic and magnetic carbon spheres-nanocomposites obtained under pressure for oxygen reduction reaction
*Jesica Castelo-Quibén, Luisa M. Pastrana-Martínez, Francisco Carrasco-Marín and **Agustín F. Pérez-Cadenas***

(11:00-11:30) COFFEE BREAK

(11:30-12:00) KEYNOTE 4
Self-consistent methodology to quantitatively analyze the phenomena taking place during operation of both EDL and sodium-ion capacitors.
***P. Przygocki**, P. Ratajczak, X. Pan, A. Chojnacka, P. Jeżowski, F. Béguin*

(12:00-13:15) ORAL SESSION 4

S4-1
Topological effects on NMR spectra of disordered carbons explored through DFT calculations
***D. Kilymis**, A. P. Bartók, C.J. Pickard and C. Merlet*

S4-2
In situ SAXS/WAXS characterisation of macroscopic yarns of carbon nanotubes (CNTf) during electrochemical processes
***C. Santos**, E. Senokos, J. Fernández-Toribio, A. Ridruejo, R. Marcilla, J. J. Vilatela*

S4-3
Low temperature performance of carbon/carbon EDLCs down to -50°C in ionic liquid binary mixture
***Emmanuel Pameté Yambou**, Barbara Górska and François Béguin*

S4-4
Electrochemical applications of UV irradiated fluorinated graphene films
***A.V. Okotrub**, V.I. Sysoev, D.V. Gorodetskii, A.V. Guselnikov, L.G. Bulusheva*

S4-5
Graphene composites as binder-free electrodes for high volumetric energy density devices
*Noel Díez, Cristina Botas, Teófilo Rojo, and **Daniel Carriazo***

(13:30-15:30) LUNCH

(15:30-16:00) KEYNOTE 5
Application of carbon microcapsules in CO_2 capture with encapsulated ionic liquids
***N. Alonso-Morales**, C. Moya, J. Palomar, J. Lemus, M. Larriba, R. Santiago, M.A. Gilarranz, J.J. Rodriguez*

(16:00-17:00) ORAL SESSION 5

S5-1
A new approach to characterization of carbon pore structure
***Jacek Jagiello** and Jeffrey Kenvin*

S5-2
On molecular simulation of phenol adsorption in slit-shaped carbons: role of carbon surface conductivity
***Z. El Oufir,** H. Ramezani, N. Mathieu, S. K. Bhatia, S. Delpeux*

S5-3
Kerogen texture modeling, adsorption and transport properties
***Yann Magnin**, N. Chanut, F. Ulm, R. Pellenq*

S5-4
Enhanced cyclic CO_2/N_2 separation performances stability on chemically modified nitrogen-doped ordered mesoporous carbon
*Ren Wei Chang, Chin Jung Lin, Sofia Ya Hsuan Liou, Miguel A. Bañares, **M. Olga Guerrero-Pérez**, Rosa M. Martín Aranda*

(17:30-22:30 approx.) VISIT TO ELCHE

Wednesday, October 23rd

(9:00-10:00) PLENARY LECTURE 2

Metal-free porous carbon catalysts for ORR: Addressing the complexity of activity governing factors
T. Bandosz

(10:00-10:30) KEYNOTE 6
How do the micropores of carbon xerogels influence their electrochemical behavior as anodes for lithium-ion batteries?
***Alexandre F. Léonard**, Marie-Laure C. Piedboeuf, Christian Balzer, Gudrun Reichenauer, Nathalie Job*

(10:30-11:30) ORAL SESSION 6

S6-1
MoS_2@CNT hybrid for free-standing charge storage: mechanistic investigations on growth and charge storage mechanism
***Moumita Rana**, Nicola Boaretto, Cleis Santos, Rebeca Marcilla and Juan Jose Vilatela*

S6-2
Silicon/biogas-derived carbon nanofibers composites: a promising anode material for lithium-ion batteries
***Ignacio Cameán**, Nuria Cuesta, Ana B. García*

S6-3
Design of Hard Carbons anodes for high performance Na-ion batteries (NIBs)
*J Conder, C Villevieille, L Simonin, **C Matei Ghimbeu***

S6-4
Mesoporous Fe-C-S composites as electroactive materials for the negative electrode of an Iron-Air battery
***N. Villanueva**, C. Alegre, M. J. Lázaro*

(11:30-12:00) COFFEE BREAK

(12:00-12:30) KEYNOTE 7
Operando analysis for charge/discharge reaction mechanism of graphite anode of Li ion battery using synchrotron radiation
***Hiroyuki Fujimoto**, Hisao Kiuchi, Shigeharu Takagi, Keiji Shimoda, Kenichi Okazaki, Zempachi Ogumi, Takeshi Abe*

(12:30-13:30) ORAL SESSION 7

S7-1
In situ X-ray photoelectron and X-ray absorption spectroscopy study of lithium interaction with fluorinated graphites
***Lyubov Bulusheva**, Yuliya Fedoseeva, Boris Senkovskiy, Andrey Chuvilin, Alexander Okotrub*

S7-2
Synthetic approaches for improving the electrical conductivity of mesoporous carbon gels
***A. Casanova**, A. Gomis-Berenguer, M.D. Calzada, C.O. Ania*

S7-3
Synthesis and characterization of graphene-related nanomaterials by catalytic chemical vapor deposition using a Co-Cu/Cellulose-Derived Carbon catalyst
*W. Henao, P. Tarifa, **F. Cazaña**, N. Latorre, E. Romeo, A. Monzón*

S7-4
Carbon microtubes derived from self-rolled chitosan acetate films and graphitized by joule heating
*A. Beda, H.Yamada, A. Egunov, C. Matei Ghimbeu, J.-P. Malval, Y. Saito, **V. Luchnikov***

(13:30-15:30) LUNCH

(15:30-16:00) KEYNOTE 8
Activated carbon monoliths from lignocellulosic biomass waste for methanol dehydration
***J.M. Rosas**, P.O. Ibeh, F.J. García-Mateos, R. Ruiz-Rosas, J. Rodríguez-Mirasol, T. Cordero*

(16:00-17:45) ORAL SESSION 8

S8-1
Biomass upgrading via H_2-free HDO using highly effective carbon-based catalysts
*J.L. Santos, J. Wei, L. Pastor-Perez, S.Gu, **M. A. Centeno** and T. R. Reina*

S8-2
Production of hydrocarbons by hydrodechlorination using functionalized carbon nanofibers
*Victor de Frutos-Ruiz, **Maria Martin-Martinez**, M. Ariadna Álvarez-Montero, Daniel Rodriguez-Franco, Juan J. Rodriguez, Luisa M. Gómez-Sainero*

S8-3
Ru, Pd, Pt as dopants of carbon nanofibers-supported Ni catalysts for one-pot cellobiose conversion
E. Frecha, D. Torres, A. Pueyo, I. Suelves, ***J.L. Pinilla***

S8-4
Noble metals supported on mesoporous biochar as a suitable catalyst for upgrading bio oils
J.L. Santos, S. Ivanova, Päivi Mäki-Arvela, Dmitry Yu. Murzin and ***M.A. Centeno***

S8-5
Templated carbons for the study of the influence of morphology, porous texture and N-doping of catalytic supports in aqueous-phase hydrodechlorination
C. Ruiz-García, ***F. Heras****, L. Calvo, N. Alonso-Morales, J.J. Rodriguez, M.A. Gilarranz*

S8-6
H_2 production on 1D and 2D Carbon-containing Fe-, Co-, and Ni-based foamy catalysts
J. Matos*, P.S. Poon, A.G. Souza-Filho, E. Barros, J.A. Rodriguez, J.C. Hernández-Garrido, E. Rodríguez-Aguado, E. Rodríguez-Castellón, M.C. Fernández de Córdoba, C.O. Ania*

S8-7
N-doping of carbon support for creation of efficient catalysts for hydrogen production from formic acid decomposition
Dmitri A. Bulushev*, Lyubov G. Bulusheva*

(18:00-20:00) POSTER SESSION 2/ COFFEE

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(20:30-22:30) CONFERENCE BANQUET

Thursday, October 24th

(9:00-9:30) KEYNOTE 9
Performance of Bi_2WO_6/carbon catalysts under real solar conditions in a CPC photoreactor
Alicia Gomis-Berenguer, Paula Muñoz-Flores, Juan Matos, ***Conchi O. Ania***

(9:30-11:00) ORAL SESSION 9

S9-1
Synthesis of hierarchical TiO_2/MWCNT photocatalysts for VOCs abatement
J. Fernández Catalá*, Á. Berenguer-Murcia, D. Cazorla-Amorós*

S9-2
Photocatalytic activity of semiconductor-free, tannin-derived mesostructured carbons
J. Matos*, Po S. Poon, V. Fierro, A. Sanchez-Sanchez, A. Celzard*

S9-3
Application of pulsed laser deposition for fabrication of carbon cloth-based free-standing bifunctional electrodes for water splitting
***Karolina Kordek**, Aleksander de Rosset, Piotr Rutkowski*

S9-4
Electrospinning of Alcell lignin for the preparation of electrodes and electrocatalysts
*Francisco José García-Mateos, **Ramiro Ruiz-Rosas**, Miguel García Rollán, Alejandro Ortega-Murcia, Emilia Morallón, Diego Cazorla-Amorós, José Rodríguez-Mirasol, Tomás Cordero*

S9-5
In-situ formation of active C-O-Fe species during the water splitting process
*Yuxiao Ding, Robert Schlögl, **Saskia Heumann***

S9-6
TiO_2-C materials prepared by hydrothermal synthesis for their application in photocatalysis
***L. Cano-Casanova**, A. Amorós-Pérez, M. Ouzzine, M.A. Lillo-Ródenas, M.C. Roman-Martínez*

(11:00-11:30) COFFEE BREAK

(11:30-12:30) HOT TOPICS ENVIRONMENT

HT5
Perspectives for carbons in environmental applications
*A. Arenillas, **T. Cordero***

HT6
Carbon monoliths with designed morphology and tailored textural properties for environmental catalytic applications
*Cristian Chaparro-Garnica, Esther Bailón-García, Agustín Bueno-López, **Dolores Lozano-Castelló***

HT7
Adsorption kinetics of nitrate ions on activated carbons
*H. Moussounda Boundzanga, B. Cagnon, C. Vautrin-Ul, **S. Bonnamy***

(12:30-14:00) ORAL SESSION 10

S10-1
Superactivated carbons synthetized by steam activation of acid-chars for pharmaceuticals removal
*Tetiana S. Hubetska, **Ana S. Mestre**, Natalia Kobylinska, José R. García, Ana P. Carvalho*

S10-2
Development of Ni catalysts supported on Cellulose Derived Carbon for CO_2 Methanation
*P. Tarifa, F. Cazaña, V. Sebastián, N. Latorre, E. Romeo, **A. Monzón***

S10-3
Effect of multi-scale texture of activated carbons and ultrasound treatment on the adsorption of carbamazepine and ibuprofen in wáter
***L Duclaux**, M. Ondarts, K. Larbi, L. Reinert, S. Guitonneau, N. Benderdouche*

S10-4
Removal of emerging pollutants present in water using an E-coli biofilm supported onto activated carbons prepared from argan wastes
Safa Benjedima**, Luis A. Romero-Cano, Mª Isidora Bautista-Toledo, Agustín F. Pérez-Cadenas, El Mostapha Lotfi, El Mahi Mohammad and **Francisco Carrasco Marín

S10-5
Simultaneous adsorption of bisphenol-a and phenol on lignin-derived activated carbons
*M.C. Gutiérrez, I. Moulefera, **F.J. García-Mateos**, J. Rodríguez-Mirasol, T. Cordero*

S10-6
Tuning the surface chemistry of carbon materials to achieve efficient Ni-based catalysts for CO_2 methanation
*L.P.L. Goncalves, J.P.S. Sousa, **O.S.G.P. Soares**, Yu. V. Kolen'ko, M.F.R. Pereira*

(14:00-14:30) CLOSING CEREMONY

POSTER SESSIONS

ADSORPTION

P1
Screening of nanoporous carbons for the storage and separation of strategic gas mixtures
*Vania Lourenço, Getaneh Gesesse, Li Zhi Guan, Huan Zhang, Encarnacion Raymundo-Piñero, M. Luisa Ferrer, Francisco del Monte, **Conchi Ania***

P2
CO_2 capture by mesoporous carbons produced from low value coal tar-derived products
*Enrique García-Díez, **Alberto Castro-Muñiz**, Fabián Suárez-García, Juan Ignacio Paredes, M. Mercedes Maroto-Valera, Susana García*

P3
Confinement Effects in the Formation of Ice/Gas Hydrate Nanocrystals evaluated using differential scanning calorimetry (DSC)
*C. Cuadrado-Collados, J. Farrando-Pérez, M. Martínez-Escandell, **J. Silvestre-Albero***

P4
Adsorption of organic compounds on lignocellulosic-derived spherical activated carbons
S. Fuster-Esteso, L. Cano-Casanova, A. Amorós-Pérez, M.C. Román-Martínez,
M.A. Lillo-Ródenas

P5
High-surface area zeolite templated carbon (ZTC) materials for methane storage
***M. Ouzzine**, J.P. Marco, H. Nishihara, T. Kyotani*

P6
Surface functionalization of activated carbon fibre from Opuntia Ficus-Indica for enhanced adsorption of herbicide from aqueous solutions
*Omar Mahi, Abdelkader Belmokhtar, **Abdelghani Benyoucef***

P7
Biochars as matrix for slow release urea
*L. V. Baia, M. A. G. de Figuereido, A. S. Luna, **A.P. Carvalho***

CARBON MATERIALS

P8
Surface functionalization of (o-phenylenediamine)-co-Aniline and these properties
*Ali Boumeftah, **Abdelkader Belmokhtar**, Abdelghani Benyoucef*

P9
Optimization of carbon structure in xerogels for different electrochemical applications
*M. Canal-Rodríguez, M.A. Montes-Morán, J.A. Menéndez, **A. Arenillas***

P10
Influence of polymerization conditions on carbon xerogels porous structure
*S.L. Flores-López, L.A. Ramírez-Montoya, J.A. Menéndez, M.A. Montes-Morán, **A. Arenillas***

P11
Synthesis and characterization of activated carbons from Algerian coal
***Wahiba Bencheikh**, Juan Jose Villora Picó, Antonio Sepúlveda Escribano, Merieme Belhachemi, Addoun Abdelhamid*

P12
Preparation and characterization of activated carbons from Baobab and Balanites shell stones and their use for diazinon removal
*L. M. Ndjientcheu Yossa, S. Ouiminga, S. Sidibe, S. Guittonneau, B. David, L. Reinert, Y. Soneda, **L. Duclaux***

P13
Waste marble dust: An interesting residue to produce cement
*A. Ruiz-Sánchez, M. Sánchez-Polo, M. Rozalen and **J. Rivera-Utrilla***

P14
A novel method for the synthesis of graphene nanostructures by atmospheric-pressure microwave plasma
***A. Casanova**, R. Rincón, J. Muñoz, A. Gomis-Berenguer, C.O. Ania, M.D. Calzada*

P15
Effect of the Isomer in the Electrochemical Incorporation of N and P Functionalities in Carbon Nanotubes
***B. Martínez-Sánchez**, A. Quintero-Jaime, D. Cazorla-Amorós, E. Morallón*

P16
Effect of electrode composition and electrolyte flow in electrochemical regeneration of activated carbon in a kilogram batch reactor
***Borja Ferrández-Gómez**, Samuel Beaumont, Diego Cazorla-Amorós, Emilia Morallón*

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A Challenge Using Classic Carbon Materials to Progress of Electrochemical Capacitors

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Carbon materials have been widely utilized for electrochemical applications as electrode active materials, conductive additives, electrode substrate, etc. The electric double layer capacitor (EDLC), an electrochemical energy-storage device with high power density, consists mainly of microporous carbon electrode and electrolyte. Activated carbons are commercially used as microporous carbon for the EDLC, but recently nanocarbons such as carbon nanotube, fullerene, graphene, templated nanoporous carbon, etc. are actively investigated in the world to enhance the capacitance and maximum charge voltage. Additionally, the nanocarbons are well designed and ordered, so the relationship between the electrochemical property and the carbon structure can be discussed clearly. However, classic carbons (classified by Inagaki and Radovic[1]) such as activated carbon, graphite, carbon black are very important from the viewpoint of industry and market scale since the productivity and cost are advantageous. Based on the above background, the author has been aiming for the breakthrough and innovation of the activated carbon for electrochemical capacitors by reference to the knowledge and findings obtained from the nanocarbons.

On this paper, the author would like to introduce a monolith-type activated carbon, "Seamless Activated Carbon[2] (**Fig.1**)" for the application as electrode of electrochemical device such as the EDLC. In the EDLC, the higher voltage operation than 3 V is required for improving the energy density and achieving more reliability, but electrochemical decomposition during high voltage charge causes the decrease in the capacitance and the increase in the internal resistance. A mechanism for this degradation by high voltage charge is the breakdown of electric network in the electrode.

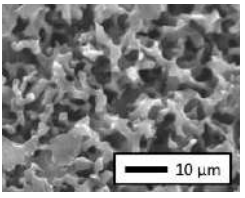

Fig. 1 Scanning electron microscopic image of seamless activated carbon.

The EDLC using the seamless activated carbon developed and commercialized by the author's laboratory and partner company, AION Co., Ltd., has good durability against high voltage charge as shown in **Fig.2**. This is due to particle-boundary free structure of the electrode. The electric network in the seamless activated carbon electrode is very stable, compared with the conventional activated carbon electrode composed of activated carbon particle, carbon black, and binder. The advantage of the seamless activated carbon electrode for other electrochemical applications such as lithium-air battery will be also addressed.

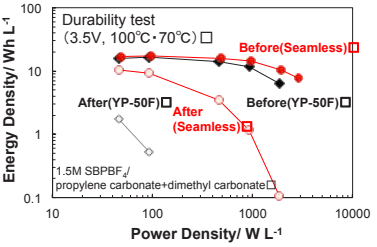

Fig. 2 Ragone plot of EDLC using densified seamless activated carbon electrode or conventional activated carbon electrode before and after durability test.

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Metal-free porous carbon catalysts for ORR: Addressing the complexity of activity governing factors

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Introduction

Owing to the high costs of Pt there is an extensive search for the replacement of Pt/C by metal-free carbons doped with various heteroatoms and functional groups. Even though nitrogen doped carbon materials are considered as promising materials to replace Pt/C highly porous carbons containing ultramicropores have not been extensively studied yet as ORR or CO_2RR metal-free catalysts. Some recent studies indicate that such factors as specific surface chemistry [1], porosity [2], surface charge [3], and defects [4] might influence the electrocatalytic reduction of O_2. Since some of these factors are related to each other, the objective of this talk is to present our resent finding on the role of surface features in this process.

Experimental

The catalytic activity for ORR was tested on commercial and synthesized porous carbons in an alkaline electrolyte. They differed in their texture, porosity, and surface chemistry. The number of electron transfer, H_2O_2 production, onset potential, kinetic current density, tolerance to methanol cross over, cycling stability and Toefl plot slop were analyzed. To link the performance to surface features the carbons were extensively characterized by N_2 adsorption, XPS, TEM/SEM, potentiometric titration and Raman spectroscopy.

Results and discussion

Majority of the carbons tested showed n close to 4 and a very small H_2O_2 production. All collected results were compared to those on Pt/C. Although the onset potential was still less positive than that on Pt/C, ultramicropores had a positive effect on the onset potential value. The measured current density was over 10 mA/cm^2. Interestingly, the highest onset potentials and n were found on N-free carbons. In this category, the carbons with a high density of oxygen groups showed an enhanced performance. These groups were found as significant for the transport of electrolyte with dissolved oxygen to small ultramicropores, crucial for ORR.

Conclusions

The results collected suggested that on porous carbons two mechanisms of ORR can exist simultaneously. One is related to heteroatom-based catalytic sites, and another- to adsorption enhanced ORR in pores similar in sizes to oxygen. The results, although focus on porosity, support importance of defects in the carbon matrix for ORR. High number of ultramicropores or oxygen groups in lager pores are certainly associated with defectous carbon surface.

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KEYNOTE LECTURES

K1

Force-driven reversible liquid–gas phase transition mediated by elastic nanoporous carbon materials

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Nano-confined spaces in porous materials enable anomalous physicochemical phenomena. In this work, we demonstrate force-driven liquid–gas phase transition mediated by elastic and soft nanoporous carbon materials, which will be suitable in high-efficiency heat management. While conventional nanoporous materials including metal-organic frameworks are mechanically hard, graphene-based nanoporous materials possess significant flexibility and enable the force-driven liquid-gas phase transition of guest refrigerants. Two types of such soft and elastic nanoporous materials are used: zeolite-templated carbon [1,2] and graphene mesosponge [3]. Compression and free-expansion of nanoporous carbon afford cooling (evaporation) and heating (condensation), respectively (Fig. 1), which are opposite to the case of the force-driven solid–solid phase transition in shape-memory alloys. The present mechanism allows the use of green refrigerants such as H_2O and alcohols, and the available latent heat is much higher than the case of the elastocaloric cooling/heating systems using shape-memory alloys. Cooling systems using such elastic nanoporous carbons potentially achieve the high coefficients of performance, by decreasing the Young's modulus of the porous materials [4].

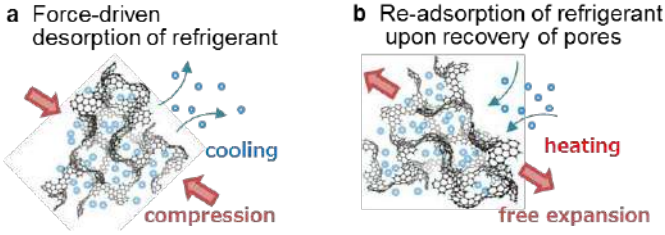

Fig. 1 Schematic of force-driven reversible liquid-gas phase transition mediated by elastic nanoporous carbon. (a) Force-driven desorption of refrigerant by compression of nanoporous carbon which adsorbs refrigerant, affording heat of desorption (endothermic). (b) Re-adsorption of refrigerant upon recovery of pores of carbon. Heat of adsorption (exothermic) is generated.

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K2

Optimizing porous carbons for supercapacitors operating in high concentrated aqueous electrolytes

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Introduction

The development of super concentrated aqueous or "water-in-salt" electrolytes represents a new strategy for developing energy storage systems able to address societal requirements in terms of environment and security [1]. The development of new electrolytes implies the adjustment of the electrode material physico-chemical properties. In aqueous electrolytes, the surface functionality plays an important role as some functionality can give additional capacitance trough pseudo-faradic reactions and/or can contribute to enhance the overpotential for H_2 evolution and therefore the stability potential window [2]. Therefore, in order to optimize the porous texture and the surface functionality of carbon based electrodes when using new super concentrated electrolytes, in the present work we present a detailed investigation of carbon/water-in-salt interface.

Experimental

Several porous carbons with different pore size distribution and surface functionalities have been tested as electrodes for supercapacitors using as electrolyte potassium acetate solutions with concentrations ranging from 1 to 30 mol Kg^{-1}.

Results, discussion and conclusions

The use of highly concentrated electrolytes allows high operating voltages in an environmentally friendly aqueous electrolyte. NMR has been used for elucidating the crucial information of the local environment of electrolyte ions at the carbon porosity. The ^{1}H NMR in Figure 1 shows that the local order of the electrolyte ions and the water molecules arrangement is different at the positive and at the negative electrode. Hence carbon material physico-chemical characteristics should be adapted differently for each electrode.

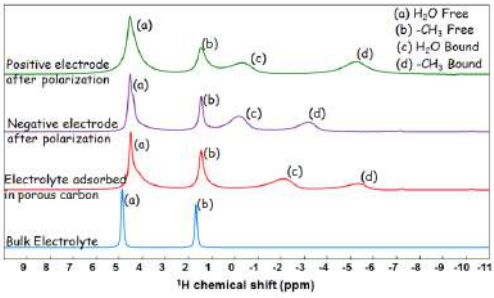

Figure 1: *^{1}H NMR spectra before and after polarization at 2.0 V*

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K3

Efficient cathodic exfoliation of graphite in aqueous electrolytes towards high quality graphene for energy and environmental applications

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Introduction

The electrochemical exfoliation of graphite in aqueous medium stands out as an attractive and scalable approach for the production of graphenes for different applications, due to its simplicity, cost-effectiveness and environmental friendliness [1]. In particular, cathodic exfoliation in water should allow access to high quality and non-oxidized graphene flakes, but this possibility has been limited by a poor intercalation ability of aqueous cations [2]. Here, we demonstrate that with a proper choice of starting graphite and electrolyte, high quality graphene flakes can be obtained in substantial yields via cathodic delamination in water.

Experimental

The cathodic exfoliation tests were undertaken in a two-electrode configuration, using a graphite piece (graphite foil) as a cathode and an aqueous solution of ammonium-based salts as the electrolytic medium, applying a negative voltage of -10V to the former for 2h.

Results and discussion

Large differences in the efficiency of a range of aqueous quaternary ammonium-based electrolytes were observed towards cathodic exfoliation of graphite foil to give high quality graphene, quantitatively compared and rationalized on the basis of their chemical structure [3]. Cathodic graphene-coated melamine foam exhibited a notable capacity towards the sorption of oils and organic solvents from water (60-150 g/g) with good re-usability (70-80% after 10 cycles) and hybrids comprised of cathodically exfoliated graphite with a small amount of vertically oriented cobalt oxide nanosheets displayed good electrochemical charge storage behavior.

Conclusions

The ability to access graphene flakes in considerable yields by the aqueous cathodic route disclosed here should raise the prospects of cathodic exfoliation as a competitive method for the industrial manufacturing of high quality graphene for energy and environmental applications.

Acknowledgements

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K4

Self-consistent methodology to quantitatively analyze the phenomena taking place during operation of both EDL and sodium-ion capacitors

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The operating voltage, and consequently energy of ECs, is limited by the electrochemical stability of the electrode/electrolyte system. During prolonged high-voltage operation of ECs (so-called floating) in aqueous neutral electrolyte, several degradation processes occur, such as electrolyte decomposition together with gas evolution and carbon electrodes surface oxidation [1-2]. Recently, electrochemical mass spectrometry (EMS) confirmed the evolution of H_2 (at the negative electrode) and CO and CO_2 (at the positive electrode), when applying CV scans or floating [2-3]. However, the level of importance between the various reactions cannot be established due to the lack of any quantitative information. The main degradation symptom of electrochemical capacitors under high voltage operation is related to the reactivity of carbon electrodes, and is accompanied by the formation of gases and decomposition products which block the porosity of carbon, with related worsening of both cell capacitance and resistance.

In this work, we present a self-consistent quantitative methodology consisting in assigning the charge passing through the electrodes to the charge spent for i) formation of gaseous products, ii) oxidation of the electrodes surface and iii) charge distribution [4]. What is more, a similar approach is used to quantitatively analyze the phenomena occurring during the operation of hybrid sodium-ion capacitors (NICs), such as e.g., sodium extraction (from carbon mixed with sacrificial materials) during charging the cells.

Acknowledgements

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K5

Application of carbon microcapsules in CO_2 capture with encapsulated ionic liquids

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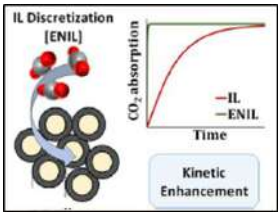
Key words: carbon microcapsules, ionic liquid, adsorption/absortion, carbon dioxide.

Carbon microcapsules have been developed using the silica template method[1]. The controlled synthesis of the template and the carbon microcapsules allow obtaining a carbon material with spherical morphology and hollow core, diameter of 400-700 nm, and shell thickness around 120 nm. The porous shell presents up to 1700 $m^2 \cdot g^{-1}$. These carbon microcapsules have been employed in different applications such as catalysis[2], smart coatings[3] and CO_2 capture[4]. Ionic liquids (IL) are promising solvents to CO_2 capture applications. The CO_2 capture can be physical or chemical absorption depending on the type of IL employed. A main disadvantage for the practical applications of ionic liquids (ILs) is the limitation in the transport properties of these solvents, which generally present higher viscosity, density and surface tension than conventional organic solvents, in particular for chemical absorption. The microcapsules were applied as solid carrier for Ionic Liquids (ILs) in CO_2 capture processes, to constitute a type of advanced materials, encapsulated ionic liquids (ENILs). The carbon microcapsules were filled with different amounts of IL up to 80%(w). This material presents a high versatility, since it can be use with different ILs, depending on the desire application.



The combination of ILs with the carbon microcapsules, that is ENILs, allowing for physical absorption exhibited the same CO_2 absorption capacity as the neat ILs, but the ENILs outperformed ILs in terms of absorption rate[5]. The ENILs also made possible to overcome main disadvantages of the ILs that capture CO_2 through a mechanism involving chemical absorption. Thus, experiments demonstrate reversibility of the chemical reaction and the efficient ENIL regeneration, mainly hindered by the unfavourable transport properties[5,6].

The application of carbon microcapsules with ILs allows from continuous to discrete liquid phase. The simulation of absorption processes based on ENILs using Aspen Plus enabled to perform a technical-economic analysis of the sorption processes in fixed bed, and to compare them with the CO_2 capture technologies currently available.

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K6

How do the micropores of carbon xerogels influence their electrochemical behavior as anodes for lithium-ion batteries?

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Introduction

In the quest towards alternative carbons for Li-ion battery anodes, hard carbons could account for increased energy density and lifetime. Such materials however still suffer from high irreversible losses during the first charge-discharge cycle though no definite relationship has been established between the type of porosity and the irreversible Li trapping. To shed some light on this issue, a synthetic carbon xerogel underwent several post-synthesis treatments in order to modulate its micropore to total pore volume ratio.

Results and discussion

The micropore volume was either expanded by CO_2-assisted physical activation or decreased using chemical vapor deposition (CVD) of a carbon layer. Materials with total surface areas between 200 and 2300 $m^2.g^{-1}$ and nearly constant macropore size and volume, were produced. Care was taken to produce electrodes that preserve the porosity of the starting materials and the variables other than the micropore texture, were carefully controlled and kept constant. The first Li^+ insertion clearly shows a linear dependency with the increase of the volume of supermicropores (0.7 – 2 nm), demonstrating the effect of micropore enlargement by activation on the storage capacity. The reversible de-insertion capacity remains constant when the maximum potential value is set at 1.5 V *vs.* Li^+/Li, but a clear linear relationship can be evidenced between the supermicropore volume and the reversible capacity if the maximum extraction potential is set at 3.0 V *vs.* Li^+/Li. As such, the contribution of the larger micropores to the Li^+ storage capacity becomes significant when cycling is performed in a wider potential window and when a water-compatible binder is used for the electrode preparation. During the first discharge, Li^+ ions penetrate massively inside the CX micropore structure, but are only partially extracted when the charge of the half-cell is performed up to 1.5 V *vs.* Li^+/Li. The increase of the potential value up to 3.0 V *vs.* Li^+/Li allows for a more pronounced de-insertion of the Li^+ ions from the microporosity of the activated CX.

Conclusions

This work shows that the pore texture of the active material-binder composites as well as the studied potential window, need to be taken into account when trying to get a more precise insight on the influence of textural parameters on the electrochemical behavior of hard carbons.

K7

Operando analysis for charge/discharge reaction mechanism of graphite anode of Li ion battery using synchrotron radiation

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Introduction

There have been many reports concerning for Li-graphite intercalation compound (Li-GIC). However, the detail discussions have not been done so far concerning the intercalation mechanism and in-plane structure of higher stage compounds. The first reason is the detection difficulty of low concentration of Li species in the higher stages. The second reason is the strong anisotropy of graphite. Such reasons make difficult to clarify the intercalation mechanism and in-plane structure. In this study, in order to elucidate the intercalation mechanism and structure change not only along *c*-axis, but also along the *a*,*b*-axes, we traced dynamically the intercalation reaction in Li-ion battery negative electrode by Operando measurement with synchrotron radiation diffraction (SRD).

Experimental

The Al-laminated half-cell composed of natural graphite and Li electrodes in 1M-$LiPF_6$/EC+EMC (3:7) was assembled. It was charged and discharged in the range of 0.01 V - 2.5 V at 0.1C during the operando measurement. The SRD was measured with BL28XU beam line at Super Photon ring-8, Japan. The exposure time was set to 10 s, and ca. 7200 diffraction profiles were obtained during the charge/discharge process. In order to analyze thus obtained enormous data in conjunction with the charge/discharge curves and their differential curves (dQ/dV), an analysis software called "Profile Chaser" was newly developed. By using the software, all the profiles of graphite electrode are loaded in the computer, and were successively displayed on a monitor synchronizing with the compositions estimated from the charge/discharge curves, so that the profile change was traced from the monitor.

Results and discussion

Fig.1 shows the profile changes of 100 and 002 diffractions of graphite in the intercalation process with the interval of 1% SOC. The structure change appeared not only in the 002 profile but also in the 100 profile. The behavior of the profile change along *c*-axis seems to synchronize with that of in-plane structure change along *a*,*b*-axes.

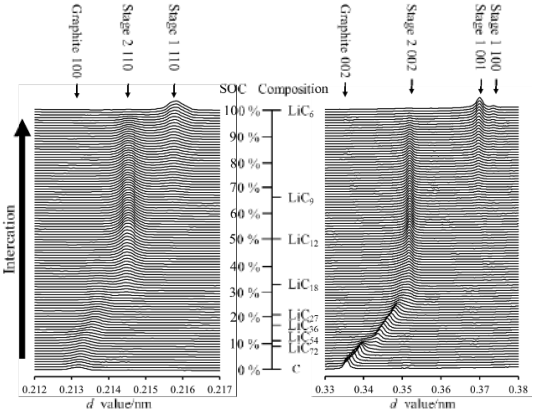

Fig. 1 The whole of the changes of 100 and 002 SRD profiles of graphite in the intercalation process.

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K8

Activated carbon monoliths from lignocellulosic biomass waste for methanol dehydration

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Introduction

The valorization of lignocellulosic biomass waste into bio-based materials, such as activated carbon materials, supposes an opportunity to obtain low-cost materials and to reduce environmental impacts. Activated carbons are usually prepared in form of powder; however, they can be present in different morphologies (powder, pellet, monolith, fiber). In the case of monolithic configurations, these materials usually present large geometric surface area, presenting, however, a low-pressure drop when they are used in fixed-bed processes with high flow rates, making them very useful materials to be used as adsorbents and/or catalysts in environmental and energy applications.

Experimental

Olive stone waste, Alcell® and Kraft lignins were used as raw materials for the preparation of activated carbon monoliths (ACMs), with a density channel of 25 cells/cm^2, by the direct extrusion of the precursors impregnated with phosphoric acid, followed by activation at 700 ºC under inert atmosphere, and washing with distilled water [1]. ACMs were characterized by N_2 and CO_2 adsorption, XPS, CO-CO_2 TPD and TGA analysis. The acidity of the ACMs was checked by isopropanol decomposition. Methanol dehydration reaction was also analyzed under air atmosphere. All catalytic tests were carried out in a fixed bed reactor.

Results and discussion

Cylindrical ACMs were obtained from different lignocelullocic waste. ACMs present well developed porosity in the micro, meso and macropore range. The main reaction for isopropanol decomposition was propylene, evidencing the acid character of the ACMs catalysts. Methanol conversions from 55 to 75%, and selectivity to dimethyl ether (DME) higher than 90% were obtained with a great stability under the operating conditions evaluated. The best results were obtained with the ACM obtained from olive stone. For this ACM, methanol conversion was reduced in the presence of water vapor, although the selectivity to DME remained very high. Furthermore, several kinetic models were evaluated to predict the methanol conversions, taking also into account the competitive influence of water vapor.

Conclusions

ACMs were prepared from direct extrusion of Alcell, Kraft lignin and olives stones particles impregnated with phosphoric acid, followed by activation and a washing step. These ACMs were used as catalysts for methanol dehydration reaction under air atmosphere, showing high conversions, selectivity to DME higher than 90% and a great stability under the operating conditions evaluated. The best results were obtained with the ACM obtained from olive stone. A kinetic model based on a LH mechanism was able to predict methanol conversions, even in the presence of water vapor.

Acknowledgements

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K9

Performance of Bi_2WO_6/carbon catalysts under real solar conditions in a CPC photoreactor

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Introduction

We have explored the impact of the incorporation of nanoporous carbons from varied physicochemical features as additives to Bi_2WO_6 for the photocatalytic degradation of a dye. Previous data at lab-scale under artificial solar light has revealed that the composition and acidic character of the carbon additive are important parameters in the performance of Bi_2WO_6/carbon catalysts, and that the carbon component improved the conversion of the dye and accelerated the degradation rate [1,2]. The presence of the carbon component also lowered the toxicity of the treated solution after short irradiation periods. The aim of this study was to evaluate the eventual scaling up of the best performing photocatalyst by analyzing the photodegradation of the dye under real solar conditions in a compound parabolic collector (CPC) pilot plant in Bio Bio region in Chile.

Experimental

The photocatalyst was synthesized by a hydrothermal treatment in the presence of a nanoporous carbon, as indicated elsewhere [1,2]. Photodegradation experiments were performed at both lab-scale using simulated solar light in a batch reactor, and at large scale in a CPC pilot plant of 30 L capacity, specifically designed for solar photocatalytic applications in Bio Bio region in Chile. In both cases a catalyst loading of 1 g/L was used. Rhodamine B was selected as target pollutant; its concentration and speciation of intermediates were followed by HPLC and spectrophotometry.

Results, Discussion and Conclusions

Data has shown that under both irradiation conditions the hybrid Bi_2WO_6/carbon catalyst outperformed the bare semiconductor, with a strong impact in the kinetics of the degradation reaction (rather than in the overall conversion). The degradation mechanism and the overall efficiency of the catalyst were strongly dependent on the irradiation conditions, with less intermediates detected in the experiments carried out in the CPC pilot plant than in the laboratory conditions (likely due to the oxygen consumption in the reactor). Interestingly, the catalyst did not show signed of deactivation upon long illumination periods, as usually obtained for conventional titania.

Acknowledgements

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ORAL COMMUNICATIONS

S1-1

A green strategy towards high-surface area carbons by chemical activation of biomass-based products with sodium thiosulfate

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Introduction

The design of new synthesis strategies for the production of porous carbons has generated growing interest due to the use of this type of material in several emergent areas such as adsorbents for gas storage, as catalysts/catalytic supports in fuel cells, and as electrodes in energy storage systems (*e.g.*, supercapacitors, batteries). In particular, the development of sustainable and green approaches is of utmost importance given that the demand for porous carbons is expected to continue to grow with the development of these technologies. Accordingly, we present a synthesis procedure for highly porous carbons based on the use of a harmless inorganic compound such as sodium thiosulfate as activating agent and an inert salt as confinement medium for enhancing the activation reactions.

Experimental

The carbon precursor was mixed by hand grinding (or freeze-drying) with KCl and $Na_2S_2O_3$. The powder was heated under N_2 up to 800 °C and held at this temperature for 1 h. Finally, the carbonized solid was washed with distilled water for several hours; the carbon particles were collected by filtration and dried [1].

Results and discussion

The activation of biomass-based substances (from simple monosaccharides like glucose/sucrose/gelatin to more complex products such as tannic acid/cellulose/sawdust) with $Na_2S_2O_3$ in the presence of KCl allows the synthesis of highly porous carbons, with surface areas of up to 2700 $m^2\ g^{-1}$ and pore volumes of up to 2.4 $cm^3\ g^{-1}$. Tuning of the pore size distribution is achieved through the modification of the $Na_2S_2O_3$/precursor weight ratio. The efficiency of this activation approach (high pore development and high activation yield) is due to the combination of two factors: i) unreacted Na_2SO_4 (formed by decomposition of $Na_2S_2O_3$) and Na_2S (formed as a consequence of the redox reactions between the carbonaceous material and Na_2SO_4) form a liquid phase at temperatures > 740 °C and ii) KCl melts at ~770 ºC, acting as confinement medium and reinforcing the contact between the solid carbonaceous matter and the Na_2SO_4- Na_2S liquid system. Besides, the porous carbons are S-doped (2-6 wt%) and dual N, S-doping can be achieved by using N-rich carbon precursors.

Conclusions

A novel, efficient, green and sustainable approach for the synthesis of S-doped highly porous carbons has been developed.

Acknowledgements

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S1-2

Low-cost biochar produced by Hydrothermal Carbonization of compost derived from Municipal Solid Waste

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Introduction

In waste processing facilities equipped with mechanical biological treatment systems, the municipal solid waste (MSW) is separated and the organic fraction is then treated by anaerobic digestion, obtaining compost that can be used as fertilizer. However, the production of compost from MBT is higher than the existing demand. This work proposes the valorization of compost derived from MSW to produced activated carbons by Hydrothermal Carbonization (HTC) [1].

Experimental

HTC was carried out in a Teflon vessel in a stainless-steel body at selected conditions (Time (x_1:1-5 h), compost load (x_2:1-4 g), temperature (x_3:150-230 ºC), 30 mL of water), that were studied through a Doehlert Matrix and Analysis of Variance. Selected responses were total organic carbon (TOC) in the liquid phase and the variation on the carbon content in solid phase.

Results and discussion

Models (Eq. (1-2)) were fitted to the experimental data, with adjusted-$R^2 > 0.94$. Likewise, ANOVA indicated reliable models (*p-values* $< 10^{-5}$ and *lack-of-fit* > 0.3). As expected, the most relevant variable for all responses is x_2. For the liquid fraction (Eq. (2)), the most relevant variable is x_3, whereas, for the carbon content (Eq. (1)), x_1 seems to play a more significant role.

$$\Delta C = C - C_0 = -0.129 - 0.035x_1 - 0.153x_2 + 0.016x_3 + 0.040x_2x_3 - 0.085x_2^2 - 0.016x_3^2 \quad (1)$$

$$TOC = 2033 + 657x_1 + 12219x_2 + 825x_3 + 364x_1x_2 + 401x_1x_3 + 376x_2x_3 - 312x_1^2 + 222x_3^2 \quad (2)$$

The highest possible retention of carbon (≈ 90%) on the solid can be achieved after 1 h of HTC and 1 g of compost at 160 ºC. At a similar condition (x_1: 1 h, x_2: 1 g; x_3: 180 ºC), TOC is predicted to achieve its minimum value (≈ 300 mg·L^{-1}).

Conclusions

Compost from MSW can be valorized through HTC to produce low-cost carbon-based materials, whose properties and quantity produced can be tailored using the developed models.

Acknowledgments

This work was supported by the project "VALORCOMP", with the reference 0119_VALORCOMP_2_P, and project "AIProcMat@N2020", with the reference NORTE-01-0145-FEDER-000006, and the Project Associate Laboratory LSRE-LCM - UID/EQU/50020/2019 - funded by national funds through FCT/MCTES (PIDDAC).

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S1-3

Recovery of graphitizable structure in activated carbons after the KOH activation process

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Introduction

Natural gas is considered a sustainable alternative energy source to substitute carbon and petroleum due to the associated environmental benefits. Activated carbons have been recognized as one of the most important materials for gas storage. The methane adsorption capacity on activated carbons depends on the porosity and their density [1]. The adsorption process is affected by the porous structure of the activated carbons. In this work two different KOH activated carbons have been heat-treated to modify their porous structure and study their methane adsorption properties.

Experimental

Two different activated carbons, PA and DO, have been prepared by KOH activation of polyaniline and a petroleum pitch. Both precursors were carbonized at 500 ºC and KOH activated at 800ºC, 1 h, using a 3:1 KOH: carbon ratio. After the synthesis, samples were heat-treated to 1000ºC-1500ºC, Samples were characterized by N_2, CO_2 isotherms, XRD, TEM, packing density, electrical conductivity and methane adsorption.

Results and discussion

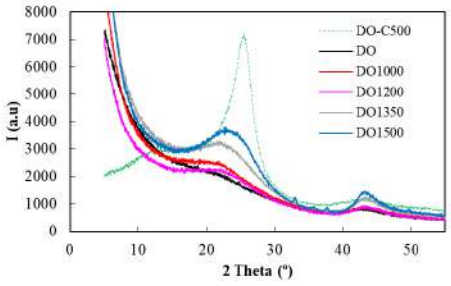

Figure 1. XRD spectra for DO series

DRX and XPS analysis showed that KOH activation process destroys the initial pregraphitic structure of the two precursors. However, the carbon obtained using the most graphitizable carbon precursor, recovers the graphitic structure to a larger extent with the thermal treatment. This fact affects to the porosity and packing density, so that the carbons obtained using DO densifies and decreases the porosity to a larger extent. This fact affects to the adsorption capacity expressed in V/V, as the amount of methane adsorbed not only depends on porosity but also on density of the carbon. Some of the activated carbon reach 180 V/V.

Conclusions

Heat treatment causes a decrease in the micropore volume but an enhancement in the density of the carbon. It is worth highlighting the high methane adsorption capacities achieved with some of these samples reach values as high as 180 V/V.

Acknowledgements

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S1-4

Synthesis of ordered mesoporous carbons by a photoinduced strategy

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Introduction

The control of the pore architectures of nanoporous carbons represents a classical challenge, in view of the multitude potential applications of such carbon materials (adsorption, catalysis, electrochemistry, drug release). As the conventional activation methods do not allow the precise control of the porosity, the development of new processes has become a largely investigated area [1,2]. Soft-template strategies for the preparation of mesoporous carbons are among the most interesting ones, as they overcome the limitations of high cost and template removal. In parallel, light is emerging as a powerful tool in material's synthesis, as it allows carrying out synthesis at ambient conditions, typically at shorter times. In this work we have explored the use of light to obtain nanoporous carbons with tuned textural features by the self-assembly of various phenolic resins.

Experimental

Various polyhydroxylated organic molecules were used as organic precursors, glyoxal as linker, and Pluronic F127 as surfactant. In a typical synthesis [3], the reactants were dissolved in ethanol and exposed to light using a 365 nm lamp. The obtained solid was pyrolysed at 600 ºC under N_2 for 2 hours. The resulting carbons were characterized by different techniques such as gas adsorption, TEM, surface pH, solid state NRM, among most representatives.

Results, discussion and conclusions

The photopolymerization of the precursors in the presence of the triblock-copolymer rendered a crosslinked matrix, without using photoinitiators or acid catalysts. The carbonization of the photopolymerized resin to obtain a nanoporous carbon showed moderate yields, ranging from 9-25 wt.%. The carbons displayed a porous structure in the micro- and mesopore range, with pore size distributions depending on the synthesis conditions. More interestingly, the carbons prepared under certain conditions exhibited an ordered interconnected mesopore structure. The use of sunlight for the photopolymerization also enabled to prepare carbon materials with a well-developed pore structure.

Acknowledgements

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S1-5

Development of Novel Pan-based Activated Carbon Fibers

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Introduction

Industrial production of Poly acrylonitrile (PAN) based carbon fiber has reached to 70,000t/y in 2018 worldwide. During this mass production, we can access to various grade of PAN carbon fiber in different prodction process, and we found some of them can be activated into activated carbon fibers (ACF). In our previous work, it was observed that the addition of nitrogen compounds to carbon raw material formed high specific surface area carbons by K_2CO_3 activation. Accordingly, we investigated both steam activation and chemical activation by K_2CO_3 of PAN fibers.

Experimental

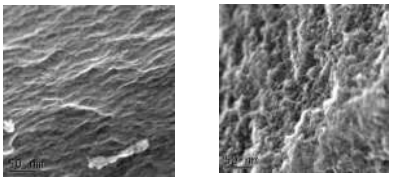
We tested various grade of PAN carbon fiber from several companies, and chose one kind of them as raw material which has stable quality and reasonable price. We did both steam activation and chemical activation at temperature over 900 degree C in the electric furnace. In the case of chemical activation, K_2CO_3 was dissolver in water and impregnated in the PAN carbon fiber. The weight ratio of K_2CO_3/Carbon fiber was set at 0.5 ~2.0. After chemical activation, the activated material was washed by water until neutral and dried till few water content. The porous properties of the products were evaluated through N_2 adsorption method at 77K by Micromeritics ASAP2420.

Results and discussion

The steam activation of PAN carbon fiber at 900~1000 degree C resulted in making ACF which has specific surface area of 400~800m^2/g. We observed adsorption rate of NO gas over PAN based ACF 2 times faster than the conventional pitch based ACF. This adsorption rate is considered to be the influence of both pore size and nitrogen functional group from PAN. The chemical activation of PAN carbon fiber is summarized in **Table 1.** We found the formation of ACF of surface area over 3,000m^2/g at the K_2CO_3/Carbon=2.0. STEM image of steam and chemical activated ACF were shown in **Figure 1.** The surface structure of these ACF were different obviously, and the chemical activation made high porosity inside the carbon fiber, which is considered as intercalation of K compounds into graphitic layers.

Table 1. Properties of Chemical Activated ACF

K_2CO_3/Carbon fiber (wt)	0.5	1.0	2.0
Specific surface area (m^2/g)	455	1025	3175
Meso pore ratio (%)	11.4	32.4	76.8



Steam activated **Chemical activated**

Figure 1. STEM image of PAN-ACF

Conclusions

The high porosity and high surface area of chemical activated ACF is seemed to be the effect of nitrogen included in the raw material PAN carbon fiber.

S1-6

Biomimetic calcium-deficient hydroxyapatite deposited on carbon fiber cloth for bone regeneration

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Introduction

Due to their multi-scale organization, breathability and biocompatibility, carbon fiber cloth (CFC) are considered as tissue engineering. However, their poor biological activity limits their extensive use in medical applications and therefore needs to be enhanced. Conversely, owing to high bioactivity, osteoconductivity and biocompatibility, calcium phosphates (CaP) have received much attention and are clinically employed either as coating or as scaffold in orthopaedics. In this field, CaP-coated carbon fiber cloth appears as promising bioceramic materials for bone regeneration.

Experimental

Coatings of CaP or strontium-substituted calcium phosphate (Sr-CaP) are deposited on CFC by sono-electrodeposition process using cathodic polarization [1]. FTIR, XRD, TEM, SEM and ^{31}P MAS NMR are performed to characterize CaP deposits. I*n vitro* investigations consisted in human osteoblast cells cultivated on the hybrid materials (CFC/CaP or Sr-CaP). For *in vivo* biological tests, biomaterials are implanted on a rat bone defect model [1].

Results and discussion

Morphology, structure and chemical composition of CaP deposits depend on of the current density or the constant potential applied at the negative electrode. For low current densities and constant potential (-1V), a plate-like carbonated calcium-deficient hydroxyapatite (CDA) is deposited, whereas at high current densities a needle-like carbonated CDA is formed. In adjusting the electrochemical conditions, Sr^{2+} can be incorporated in the CDA phase [2]. Biological tests through *in vitro* osteoblast culture evidenced a strong interaction with cells and an increase of cell density and proliferation with Sr^{2+} incorporation in the CDA structure. For *in vivo* biological tests, the setting of the hybrid material on a bone defect shows a significant acceleration of the bone regeneration. Furthermore, drugs were introduced in each component of the CaP/CFC material accounting for interesting medical applications.

Conclusions

Different types of microtexture, structure and chemical composition of CaP deposits are formed through variation of electrochemical parameters. At -1V, the deposit consists in a homogeneous biomimetic plate-like carbonated CDA. Investigation of CaP characteristics shows that the CDA deposition mechanisms are governed by the water electrolysis rate. The substitution of Ca^{2+} ions by Sr^{2+} ions is evidenced. The sono-electrodeposition is shown to be a versatile process bringing new insights. An increase of cell viability and proliferation is emphasized in Sr-CaP/CFC materials. I*n vivo* tests validated the potential of these biomimetic materials as bioactive scaffold for bone regeneration.

Acknowledgements

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S2-1

Capacitance vs. current density in microporous carbon monoliths

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Introduction

Carbon monoliths are binder-free and self-standing pieces of carbon that can be used theirselves as electrodes for supercapacitors. Compared to compacted pellets made from carbon powder and a binder, the monoliths show better performances [1-3]. In this work, the capacitance rate is studied on the basis of the electrical conductivity and porosity of the monoliths, the type of electrolyte (H_2SO_4 or KOH) and its ionic conductivity.

Experimental

Three commercial carbon monoliths (T3, T4 and T5) were transformed into the heat-treated monoliths (T3t, T4t and T5t, respectively) after heating at 750 ºC under N_2 flow. Their surface chemistry was characterized by TPD. Their specific surface areas (BET and DFT) and pore size distributions (PSDs) were also determined. The electric conductivity of the monoliths and the ionic conductivity of the electrolytes were measured at room temperature. 2M H_2SO_4, 1M KOH and 6M KOH were the chosen electrolytes. The electrochemical study was carried out in a three-electrode cell in which the monoliths were the working electrodes.

Results and discussion

The thermal treatment does not affect the electric conductivity of the monoliths, but increases the specific surface area and changes slightly the PSD. All the monoliths are microporous carbons with narrow PSDs in the 0.5-0.8 nm range. T4 and T4t monoliths show larger mean micropore sizes, which agree with their higher capacitance rates. The monoliths working as negative electrode (cations involved) and as positive electrodes (anions involved) are studied. The capacitance rate depends on the ionic conductivity of the electrolyte, following the trend 6M KOH > 2M H_2SO_4 > 1M KOH.

Conclusions

Higher capacitance rates are observed for the monoliths functioning as negative electrode (H_3O^+ and K^+) than as positive electrode (HSO_4^- and OH^-). These results are of interest for designing asymmetric and hybrid supercapacitors. The pore range of 0.6-0.8 nm is sufficient for obtaining high capacitance rate for H_3O^+, K^+ and HSO_4^- but not for OH^-, which requires pores bigger than 0.8 nm. The electric conductivity of the monoliths, which is high enough, has no effect on the capacitance retention. However, the increase of the ionic conductivity of the electrolyte by increasing its concentration leads to an increase of the capacitance rate.

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S2-2

Carbon monoliths with an ordered mesoporous structure from coal tar-derived products for electrochemical energy storage

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Introduction

In the conventional preparation of electrodes from carbon materials for electrochemical energy storage devices, the carbon component is mixed with a binder and a conductive additive, which are essentially inactive materials and therefore their use should be ideally avoided. In this work, binderless carbon monoliths with an ordered mesoporous structure were obtained, this being a very uncommon feature of such carbon materials, and we tested them as electrodes for supercapacitors.

Experimental

The materials were obtained by hard templating, using a mesoporous silica as template (SBA-15 and KIT-6), and creosote, a low-value product of the distillation of coal tar, as the carbon precursor. The template was infiltrated in acidic medium, and the resulting creosote-template composites were pressed at 1 ton to obtain disk-shaped monoliths. The monoliths were then carbonized under argon, and finally the template was removed by washing with 1 M NaOH. The monoliths retained the original disk shape.

Results and discussion

Monoliths obtained from both SBA-15 and KIT-6 showed a well-developed ordered mesoporous structure with a very narrow pore size distribution and a surface area of 1015 and 856 m^2/g, respectively. The capacitance values exhibited by the two monoliths were very similar and as high as 188 F/g, recorded at a current density of 50 mA/g in 1 M H_2SO_4 electrolyte in a 3-electrode cell configuration. This value was a 30% higher than that of their respective powder counterparts, from which paste electrodes (sample:binder:carbon black=85:10:5) were prepared and tested. Furthermore, the monoliths showed a better capacitance retention at high voltage scan rates and high current densities than the one obtained with a paste electrode prepared with YP-50F as the active material, 142 F/g (the capacitance values were normalized to the total weight of the electrodes including the additives used in the preparation of the paste).

Conclusions

Ordered mesoporous carbon monoliths were obtained without adding any binder, showing a good mesoporous structure and textural properties. The monoliths are very promising as electrodes for supercapacitors.

Acknowledgements

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S2-3

Utilization of whey for the synthesis of nitrogen doped carbon xerogel supercapacitors

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Introduction

The whey is a by-product obtained in the cheese and casein production process that can be used for several applications. Due to the large annually volumes of whey produced, its final disposal represents a serious environmental and economic problem. On the other hand, resorcinol (R) / formaldehyde (F) carbon xerogels have shown great interest to be used as electrodes of supercapacitors since their porosity, structure and chemistry can be modulated by controlling the synthesis conditions[1]. In this sense, the use of whey as solvent in the precursor formulation allows to use a low cost product as reactant in the polymerization process, at the same time to introduce some desired heteroatoms into the gel structure.

Experimental

Two different formulations of R/F organic xerogels (OX) where synthesized varying the final pH of the precursor solution (4.1 and 6.5) and setting constant other chemical variables (R/F ratio, dilution, % MeOH). In both cases, liquid whey, instead of water, was used as solvent during the polymerization reactions. After a sol-gel process assisted by microwave heating, followed by curing and drying steps, the OXs were obtained and subsequently activated under oxidative atmosphere (100 mL/min of CO_2 at 1000 ºC) in a tubular furnace. The activated carbon xerogels (AX) were finally characterized and tested as electrodes in aqueous supercapacitors.

Results and discussion

The liquid whey has a 10.7 % of solid residue with a nitrogen content of 2.1 wt% that can be incorporated to the gel structure. The AX synthesized using whey as solvent show a large specific surface area of 1172 and 1469 m^2g^{-1} for AXW4.1 and AXW6.5 respectively, which are analogous to the reference gel (AX6.5) synthesized using water, but showing nitrogen content (1.0 %). The incorporation of nitrogen into the gel structure makes a notably increase in the electrical conductivity of the samples.

Conclusions

The use of whey instead water during the synthesis of the organic gel works as a low-cost nitrogen source allowing the generation of highly porous carbon xerogels with nitrogen content that makes them suitable for use as electrodes in aqueous supercapacitors.

Acknowledgements

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S2-4

Cellulose-based activated carbon fibers for use as supercapacitor electrodes

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Introduction

Global energy consumption has accelerated alarmingly due to the rapid development of the global economy and the growing world population.[1-3] To meet the growing energy demand needed to maintain today's standard of living while avoiding resource depletion and pollution, it is necessary to develop efficient, cost-effective and environmentally friendly energy sources.[2,3] Research efforts are currently focused on improving the performance of energy storage devices, e.g. supercapacitors. Carbon-based materials have attracted great interest in the application as supercapacitor electrodes due to their frequency, chemical and thermal stability, processability, and the ability to adapt their structural properties. Activated carbon materials in particular are characterized by their large surface area (>1000 $m^2 g^{-1}$) and their pore volume (>0.5 $cm^3 g^{-1}$) at relatively low costs.

Experimental

Viscose fibers (1.7 dtex, 38 mm) were impregnated in a diammonium hydrogen phosphate (DAHP) solution with different concentrations. After drying, the fibers were carbonized in a chamber furnace at different temperatures and heating rates according to a design of experiment and then activated by CO_2 at different temperatures, activation times and gas flows. The resulting activated carbon fibers (ACFs) were analysed and tested using Nitrogen adsorption/desorption isotherms, spectroscopic methods and electrochemical testing utilizing a three-electrode setup (cyclic voltammetry, galvanostatic charge- & discharging and impedance spectroscopy).

Results & Conclusions

Viscose fibers are well suited as precursors for electrode materials. Through the statistical approach the process could be optimized for yield, pore size distribution (PSD) and thus the specific capacity of the produced ACFs. High surface areas up to 3200 $m^2 g^{-1}$ were obtained. By using DAHP the yield could be increased significantly and a PSD resulting in a specific capacity of up to 170 F g^{-1} was achieved. The cycle stability was 96 % after 10 000 cycles.

Acknowledgement

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S3-1

Fe-N-doped hydrothermal carbons for the oxygen reduction reaction

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Introduction

Nowadays, fuel cells are presented as efficient energy conversion devices with a promising potential owing to their high power density and negligible pollutant emissions. However, the overall kinetics of these devices are still hindered by the reaction that takes place at the cathode: the oxygen reduction reaction (ORR). Therefore, the development of new electrode materials is essential to improve the kinetics of the ORR. In this study, different strategies to introduce iron and nitrogen functionalities into the structure of carbon materials have been evaluated.

Experimental

Different carbons were treated with melamine to incorporate nitrogen functionalities and impregnated with iron (II)phthalocyanine (FePc) to add iron nanoparticles. All materials were tested as electrocatalysts for ORR and the relationship between the final properties and the ORR performance was evaluated.

Results and discussion

The onset potential was improved and the two-electron mechanism of the pristine carbons was shifted closer to a four-electron pathway due to the presence of nitrogen. Interestingly, the high pyridinic content related to a high ratio of pyridinic/quaternary nitrogen increases the onset potential, while a decrease in the quaternary/pyrrolic nitrogen ratio favors an increase in the number of electrons [1]. In addition, the Fe-N complex improves the catalytic performance as iron acts as main active sites.

Conclusions

The surface chemistry of carbon materials was successfully modified by the incorporation of nitrogen and iron in the carbon matrix. The tuning of the proper proportion between the different nitrogen functionalities is a key factor to improve the electrochemical performance of the carbon electrocatalysts, especially concerning the mechanism of the reaction. In addition, the incorporation of iron in the form of macrocyclic compound improves the onset potential of the materials, demonstrating that the adequate combination of the chemical properties can make non-noble metal carbons competitive electrocatalysts towards ORR.

Acknowledgments

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S3-2

Porous activated binderless pellets for electrochemical oxygen evolution reaction

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Introduction

Traditionally, noble metal catalysts (Pt, Ru, Ir) or transition metals and metal oxides (Ni, Co) have been considered as the best electrocatalysts for the oxygen evolution reaction (OER) due to its high activity.[1] However, the high cost, scarcity, and poor long-term stability of these noble metal-based catalysts significantly hinder their large-scale applications.[2] In this sense, metal-free carbon catalysts have attracted much attention in these energy conversion and storage technologies because of its good electronic conductivity and high activity, in addition to their low-cost.[3] In order to produce porous carbon materials, hydrothermal carbonization of glucose solution combine with a templating strategy was selected to obtain materials with a mesoporous structure. The materials were obtained in a pellet morphology.

Results and discussion

Cyclic voltammetry at high anodic potential were carried to measure the OER activity of the carbon pellet (Figure 1a) in basic electrolyte (0.1 M KOH). The higher oxidation current comes from not only oxygen evolution by oxidizing water, but also carbon oxidation from the carbon pellet. Thus, we also considered the stability of the porous pellets at OER by applying a current density to observe the change of the overpotential at highly oxidative conditions. As can be observed from Figure 1b, the materials exhibited an enhanced on the electrocatalytic activity and a good durability (Figure 1c).

To conclude, we have presented the synthesis of porous activated carbon materials in the form of a pellet without the employ of any binder that can be employed as OER electrocatalysts.

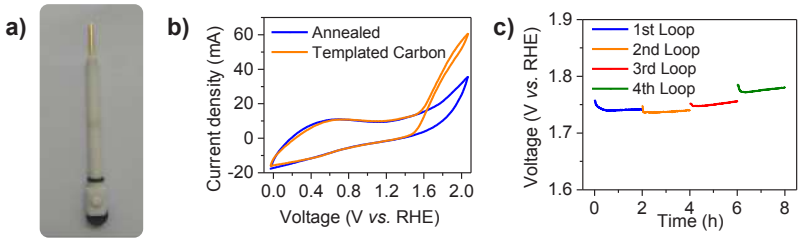

Figure 1. a) Image of the pellet in the holder, b) comparison of the cyclic voltammetries in 0.1 M KOH at 5 mV s^{-1} for templated porous carbon and carbonized pellets and c) stability of the templated porous carbons by applying a current density of 10 mA cm^{-2}.

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S3-3

Synthesis of N-doped graphenic foam for the oxygen reduction reaction in PEMFC

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Introduction

Proton exchange membrane fuel cells (PEMFC) have attracted worldwide research because of their advantages including zero emission of greenhouse gas and high energy efficiency. At the current technological stage, platinum-based nanoparticles supported by microporous carbon materials are the most efficient catalysts. However, they induce a high cost and are very sensitive to the supply gas pollution. Nitrogen-doped graphenic materials have been shown to be electroactive materials thanks to the difference of electronegativity between carbon and nitrogen atoms, inducing a redistribution of the electric charges of the atoms. Moreover, molecular dynamic simulations [1] have shown that addition of nitrogen atoms inside the graphene network could catalyze the sluggish oxygen reduction reaction (ORR). The use of this material could be a real asset for the democratization of the PEMFC.

Experimental

Our group has been working on preparation of graphenic foams, an innovative material combining the properties of graphene with those exhibited by a three-dimensional microporous structure with a specific surface greater than 2000 m²/g [2]. The elaboration of a nitrogen-doped graphene foam has been developed from the previous studies on N-free graphenic foam, using an original solvothermal-based process involving cyclohexanol, ethanolamine and sodium, followed by a thermal treatment.

Results and discussion

A crystallized graphenic material with a 3D-shape has been obtained, showing a polycrystalline assembly of nanometric graphene sheets containing a nitrogen load between 1.0 at. % and 3.0 at.%. XPS analysis have shown that 90 at. % of the nitrogen atoms were successfully inserted in the graphenic network in the form of pyrrolic, quaternary and pyridinic functions which is promising for the targeted ORR.

Conclusions

This new method has permitted to synthetize a nitrogen-doped graphenic foam with success. Further structural, textural and electrochemical characterizations are currently carried out to test the potential of these materials for the ORR catalysis – without addition of platinum – and their application in PEMFC.

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S3-4

Recycling the Spent Bleaching Earth Waste Material into Electrocatalytic Component

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The design of electrocatalytic materials with high efficiency and without noble metals for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are essential for the development of new emerging electrochemical energy storage and conversion devices [1]. Spent bleaching earth (SBE) is a worthless oil refinery waste material containing a notable percentage of residual oil. New applications are urgent such as converting SBE into catalysts, according to the circular economy concept.

In this work SBE has been used as electrocatalytic component for the reversible oxygen electrode. SBE was chemically treated to obtain based-carbon compounds. Then, cobalt, iron and/or tungsten heteropolyacid were added to the carbon-based SBE compounds to obtain different composites. The textural, structural and surface chemistry properties of the composites materials were analysed along with electrochemical characterization in a three electrode cell in alkaline medium.

Electrochemical results evidenced Co/SBE catalyst proved to be a valuable bifunctional competitor for ORR and OER showing activity in both reactions (Figure 1) and a better stability than Pt in accelerated tests.

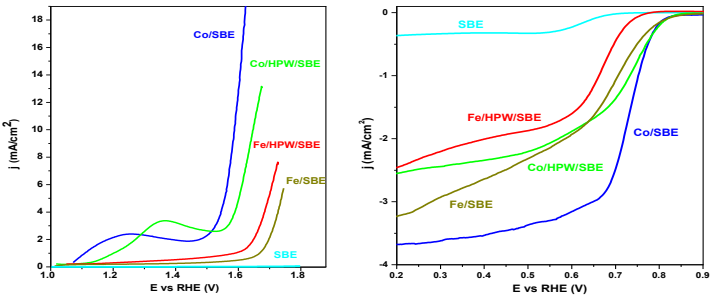

Figure 1. OER polarization curve in 0.1 M NaOH at 1600 rpm, 10mVs^{-1}(left); ORR polarization curve in O_2 saturated 0.1M NaOH at 1600 rpm, 10mVs^{-1}(right).

Acknowledgements

By the Spanish Ministry of Science, Innovation and Universities, through project ENE2017-83976-C2-1-R (co-founded by FEDER), the Spanish National Research Council (CSIC) through project iCOOP20202 and MERC grant project 99392002. D. F.I. also thanks the CSIC for his JAE-Intro grant.

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S3-5

How to make a proper 3D characterization of PEMFC catalyst layer?

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Introduction

The coating technique and the type of carbon support can strongly affect the homogeneity and the thickness of the catalyst layers of proton exchange membrane fuel cells. These features can in turn modify the local diffusion properties of the layer and the final cell performance, but literature about catalytic layers does not often address such issues. This work aims at studying the topography of PEMFC catalyst layers by means of 3D characterization methods.

Experimental

Two types of slurries, made of Nafion® and carbon black or carbon xerogel, have been coated on Kapton® by film-casting and by spray-coating. The surface topography of the samples was characterized by contact profilometry and 3D laser scanning microscopy.

Results and discussion

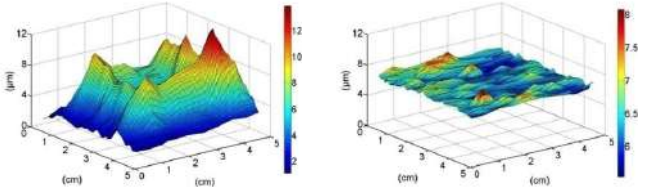

Figure 1: Example of profilometry measurements. Carbon black. Left: Film-casting. Right: spray-coating.

Contact profilometry allows to perform measurements over the entire surface of the sample while only a small part of the sample was analyzed (0.25 cm^2) with a high definition with 3D microscopy, due to much longer observation times required. The results obtained from profilometry (Figure 1) show, for instance, that spray-coating leads to better reproducibility and homogeneity of the average thickness; however, the surface is characterized by a higher roughness. 3D microscopy allowed to observe large µ-sized xerogel particles. Overall, it has been shown that measurements by 3D laser microscopy lead to more accurate thickness values compared to contact profilometry in the case of rough samples. Finally, comparison between the two techniques show that contact profilometry measurements overestimate the thickness in the case of rough samples; in that case, corrections have to be applied.

Conclusions

- Necessity to control the thickness on the whole surface of coating for PEMFC.
- Set up easy and effective of this method of characterization.
- Profilometry measurements overestimate the thickness in the case of rough coatings.

S3-6

Graphitic and magnetic carbon spheres-nanocomposites obtained under pressure for oxygen reduction reaction

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Introduction

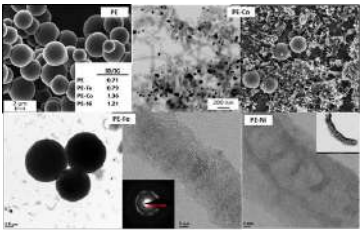
The unstoppable growth in energy demand has encouraged intensely the researching on alternative energy conversion and storage systems highly efficient which have to be adequately addressed to maintain the sustainability of our environment. In this regard, the Fuel Cells are generally considered one of the most promising solutions because of their competitive advantages.

Experimental

0.5 g of LDPE and the corresponding amount of the metal precursor salt (Fe, Co or Ni) were placed and treated at 700 °C into a closed hand-made Hastelloy® reactor of 25 mL capacity. The heating rate was 10 °C/min with a dwell time of 2 h at the target temperature.

Results and discussion

Carbon microspheres (CS) were obtained in all cases. The presence of metal provokes the development of carbon nanofibers with different sizes and shapes on the CS. All materials present high degree of graphitization, especially the metal-free sample, pointed out by the small ratio ID/IG (Raman). The spherical shape as well as the high degree of graphitization are attributed to the effect of the generated pressure since previous studies related to plastic waste pyrolyzed into an open reactor, the presence of carbon microspheres was not found [1]. The metal-free material (PE), is able to accomplish the ORR by the 2-electron pathway, but the reaction starts at -0.30 V that is the highest potential compared to the others. When some of the metals are present, the electro-catalytic activity improves considerably, all metal-samples present lower E_{ONSET}, improved kinetics and they are able to transfer more electrons.



Sample	E_{ONSET} (v)	j_k mAcm^{-2}	n
PE	-0.30	2.65	2.0
PE-Fe	-0.24	6.40	3.8
PE-Co	-0.26	12.65	3.1
PE-Ni	-0.20	4.64	2.3

Conclusions

The present work reports the successful obtaining of highly graphitic and magnetic carbon microspheres from LDPE by a facile one-step method under solvent-free conditions. Not only the metal content but also the carbon nanostructures developed in these composites, can influence the electro-catalytic activity leading to a 4-electron pathway.

Acknowledgements

This research is supported by the projects RTI2018-099224-B-I00 and RMN-172

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S4-1

Topological effects of NMR spectra of disordered carbons through DFT calculations

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Disordered carbons are being used as supercapacitor electrodes and their capacitance has been shown to dramatically improve when their pore size reaches the nanometer range [1]. Being able to thoroughly understand the atomic-scale structure of such materials can lead to the design of electrodes with higher performance and the optimization of fabrication protocols. NMR spectroscopy is an important method for the characterization of disordered carbons [2], however it is still not completely clear how the spectral characteristics correlate to the local topological motifs in these materials. In this work we present the results from a series of DFT calculations of isotropic NMR shieldings on periodic systems with varying densities and then correlate them to structural descriptors. We show that the isotropic shieldings correlate to the atomic coordination number, as well as to the presence of defect rings around a given atom. On the other hand, we show that the isotropic shieldings do not seem to have a direct dependence on the system density.

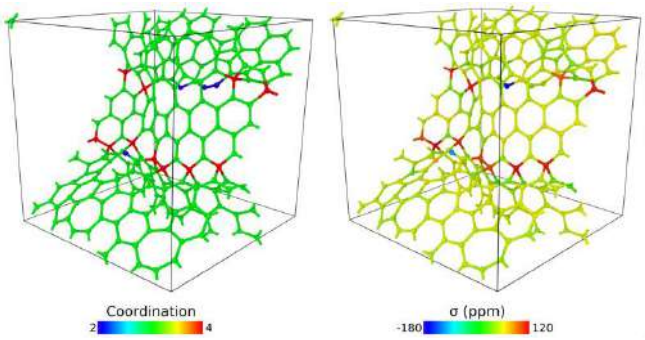

Figure: Coordination number for carbon atoms in a disordered carbon (left) and the corresponding isotropic shieldings (right).

Acknowledgements
This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement no. 714581). This work was granted access to the HPC resources of CALMIP supercomputing center under the allocation P19003.ext

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S4-2

in situ SAXS/WAXS characterisation of macroscopic yarns of carbon nanotubes (CNTf) during electrochemical processes

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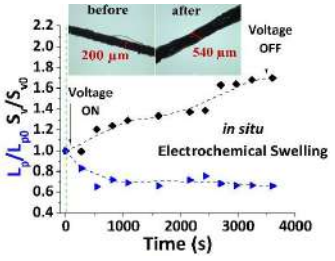
Introduction

The hierarchical structure of macroscopic yarns of carbon nanotubes (CNTf) is at the centre of a wide range of charge storage and transfer processes when CNTf are used as electrodes and/or current collectors. In this work, we have introduced a method based on *in situ* small and wide X-ray scattering (SAXS/WAXS) characterisation of CNTf during electrochemical processes.

Experimental

2D WAXS/SAXS patterns (λ=1 Å) were collected at ALBA synchrotron facilities at NCD-SWEET Beamline 11. Electrochemical studies (i.e. swelling process in Pyr14TFSI, and ion's tracking in aqueous electrolytes) were performed using a Biologic SP-200 potentiostat-galvanostat, in a three-electrode configuration.

Results and discussion



WAXS/SAXS measurements confirm the highly-crystalline, yet porous and hierarchical structure of CNTf. However, there is a scattering component due to density fluctuations, DFs (i.e. imperfect packing of graphitic planes). Thus, accurate structural descriptors (surface area, average pore size and bundle size) are determined after correction for scattering from DFs. *In situ* WAXS/SAXS during the electrochemical swelling provide continuous monitoring of the increase in effective surface area caused by electrostatic separation of bundles, that is in agreement with *ex situ* capacitance measurements. Moreover, different charging/discharging mechanisms can be identified thanks to the *in situ* combination of X-ray transmission data, from the photo-diode of the beamline, and SAXS profiles as a function of the voltage of the working electrode.

Conclusions

This work probes the powerful combination of *in situ* X-Ray from synchrotron light and electrochemical studies by showing *1)* fundamental properties of these materials in ionic liquids (i.e. surface modification),[1] *2)* the effect of the ions' electrosorption in aqueous electrolytes upon applying potential.

Acknowledgements

The authors are grateful to the stuff of NCD-SWEET beamline (ALBA Synchrotron) for their assistance with the WAXS/SAXS measurements.

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S4-3

Low temperature performance of carbon/carbon EDLCs down to -50°C in ionic liquid binary mixture

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Ionic liquids (ILs) are a solvent-free perspective class of electrolytes for high voltage electrical double-layer capacitors (EDLCs). They are characterized by high electrochemical stability, as well as they are neither volatile nor flammable. Therefore, ILs are superior to conventional organic electrolytes, e.g., 1 mol L^{-1} $TEABF_4$ in acetonitrile, which pose safety and toxicity concerns. However, the relatively high melting point of ILs restricts the scope of their applicability at low temperature compared to traditional EDLCs performing from -40 °C up to +70 °C. To overcome these limitations and to extend the operating range of EDLCs with ILs to sub-ambient temperature, their binary mixtures have been proposed as electrolytes [1]. Recently, a graphite oxide-based EDLC incorporating a binary mixture (1:1 by molar ratio) of 1-butyl-4-methyl-pyridinium tetrafluoroborate ($BMPBF_4$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIBF_4$) could perform even down to -50 °C [2]. Nevertheless, as graphite oxide has a relatively low density, the resulting volumetric capacitance of such EDLC is very low.

In this work, binary mixtures with various molar ratios were formulated using two ILs with a common 1-ethyl-3-methylimidazolium cation, $[EMIm]^+$, coupled with bis(trifluosulfonyl)imide $[FSI]^-$ or tetrafluoroborate $[BF_4]^-$ anions. Their thermal properties, viscosity and conductivity were determined. Accordingly, the $(EMImFSI)_{0.5}(EMImBF_4)_{0.5}$ mixture, which was liquid down to -97 °C as well as displayed relatively low viscosity of 33.0 mP s and relatively good conductivity of 12.1 mS cm^{-1} (at 20 °C), was selected as electrolyte for carbon-based EDLCs.

To uphold the low-temperature performance of capacitors, we applied electrodes made of mesoporous materials: carbon black SC2A (by Cabot) and a home-made templated carbon MP98B with mesopores (average size of 3.5 nm) well-fitted for the electrolyte ions. Both EDLCs operated down to -50 °C, while the cell based on MP98B exhibited better charge propagation and greater capacitance (140 F $g^{-1\dagger}$ vs 115 F $g^{-1\dagger}$ @ 20 °C).

During the presentation, the electrochemical properties of EDLCs at low temperature will be discussed in light of the porous texture of carbons and thermal properties of IL mixtures.

†capacitance values are expressed per average active mass in one electrode.

Acknowledgements
The Polish National Science Center (NCN) is acknowledged for supporting the MAESTRO project UMO-2016/22/A/ST4/00092.

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S4-4

Electrochemical applications of UV irradiated fluorinated graphene films

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Chemically modified graphene is a promising basis for the manufacture of elements of flexible electronics, such as microcapacitors, sensors, sorbents, etc. Fluorinated graphene (FG), which can be dispersed in organic solvents, shows high stability as a matrix for forming a separating layer in microdevices. There are a number of chemical and physical methods for the removal of fluorine atoms from the surface of fluorinated graphite, which allows you to create areas with a given degree of conductivity. In this work, we produce thin films from fluorinated graphene and complete remove fluorine atoms surface by irradiation of low power laser (λ = 380 nm).

The fluorinated graphites with composition C_2F_x were synthesized using low temperature fluorination by BrF_3 from natural graphite. Suspension of FG in toluene was used to produce films having a thickness of 1 - 10 μm. The focusing UV radiation treatment converted the FG to graphene. Electronic states of recovered fluorinated graphene surface investigated by Raman, XPS and NEXAFS methods. Testing of capacitors with a thickness about 5 μm demonstrated specific capacitance values up to 10 mF/cm^2.

We design a sandwich-type electrochemical cell consisting of graphene as a working electrode, phosphoric acid impregnated FG film as a separator wetted with electrolyte, and conducting back electrode in order to investigate the processes occurring at a graphene/electrolyte interface. *In situ* XPS measurements are used for revealing the influence of positively and negatively polarized double layer at graphene surface on electronic state of the graphene. Quantum-chemical calculations confirm our experimental results, showing significant charge transfer under adsorption of proton and phosphate anion on graphene.

According to XPS data, we detected the splitting of C 1s core level of graphene electrode at discharged and charged states of electrode and described them in terms of energy change of Fermi level and charge transfer at the electrode/electrolyte interface under ion adsorption. An application of potential to graphene shifts the C 1s line and changes relative positions of the components. The study demonstrates the prospects the use of FG films impregnated by phosphoric acid as a solid electrolyte in microsupercapacitors and the approaches for *in situ* probing the electronic state of graphene/electrolyte interfaces.

Acknowledgements
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S4-5

Graphene composites as binder-free electrodes for high volumetric energy density devices

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Introduction

The rapid development of portable electronic devices, such as tablets and cell phones which incorporate complex applications and functionalities, requires new compact energy storage devices with improved volumetric energy and power densities.

Herein, we present some strategies for the preparation of different reduced graphene oxide composites with a high density of 1.5 g cm^{-3}. These graphene-based wafers are easily prepared by the solvent casting of an ethanolic suspension of graphene oxide containing a certain amount of silicon nanoparticles and then thermal reduction at 1000 ºC, or by the hydrothermal reduction of an aqueous suspension of graphene oxide and carbon nanotubes, which yields monolithic hydrogels that can be finally compacted under pressure. The potential of these self-standing films was electrochemically evaluated as binder free electrodes in lithium ion batteries and supercapacitors.

Results

The results show that silicon containing films exhibit very good stability over the first 100 cycles, high Coulombic efficiencies and high reversible volumetric specific capacity (~1100 mAh cm^{-3}) as anode in lithium ion batteries.[1] On the other hand, the use of graphene-carbon nanotube composites as electrodes for electrochemical capacitors show that the incorporation of just a 2 wt.% of carbon nanotubes into the graphene-based wafer produces a significant enhancement of the capacitance retention at high current densities when compared to its counterpart without carbon nanotubes. This improvement, which is due to a higher electrode surface area accessible to electrolyte ions and to the partial alleviation of ion diffusion restrictions, was especially relevant in those systems using electrodes with large mass loadings. Thus, volumetric capacitance values of 255 F cm^{-3} at 1 A g^{-1} and very good rate capability (185 F cm^{-3} at 10 A g^{-1}) were achieved even using electrodes with a mass loading as high as 13 mg cm^{-2}.[2]

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S5-1

A new approach to characterization of carbon pore structure

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Introduction

For years, the characterization of carbon pore size distribution (PSD) has been dominated by the analysis of nitrogen (N_2) isotherms measured at its boiling point (77 K). However, N_2 is not the most appropriate molecular probe for the PSD analysis because of its significant quadrupole moment that may influence the N_2 adsorption due to its interactions with polar surface sites. For this reason, IUPAC Technical Report 2015 recommended Ar as more reliable for the PSD analysis. We have recently proposed using O_2 instead of N_2 or Ar [1] as the quadrupole moment of O_2 is less than 30% of the N_2 value. Moreover, we demonstrated a quantitative agreement between the PSD results derived from the adsorption isotherms of O_2 and N_2 measured at 77 K, and Ar at 87 K on representative carbon samples.

The same IUPAC report recommended using CO_2 at 273 K for the analysis of ultramicroporous carbons because at this temperature CO_2 diffuses faster into micropores than N_2 at 77 K. This recommendation, however, is inconsistent with the fact that the quadrupole moment of CO_2 is even larger than that of N_2. To improve the diffusion into ultramicropores, we propose in this work to use H_2 in combination with O_2 isotherms measured at 77 K. H_2 molecule has a very small quadrupole moment and smaller diameter than CO_2.

Results and discussion

In this work, we use 2D-NLDFT models to simultaneously analyze H_2 and O_2 isotherms measured at 77 K. We show comparisons of PSD results derived from single isotherms and the dual analysis of both isotherms. The approach introduced in this work is advantages compared to the earlier presented "dual analysis method"[2] based on N_2 and CO_2 isotherms, because of the lower quadrupole moments of O_2 and H_2. It is also more practically convenient because of the same cryogen, liquid N_2, used for both analyses. An example of using the dual isotherm analysis of O_2 and H_2 (Fig. 1) demonstrates a quantitative agreement between PSDs calculated from a single O_2 isotherm in the range of (10^{-7}-1) p/p_0 and a partial O_2 isotherm in the range of (10^{-3}-1) p/p_0 combined with H_2 isotherm in the range from 10^{-3} to 1.0 atm.

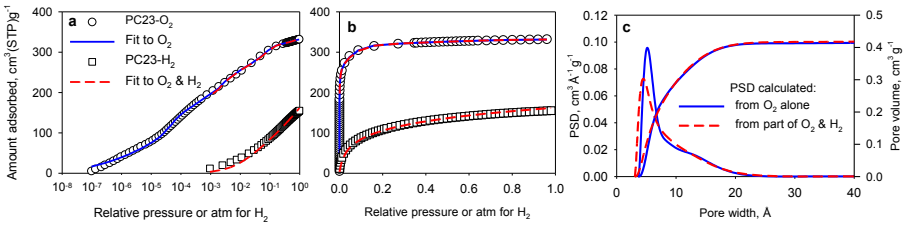

Fig. 1. PSD analysis of microporous carbon PC23 using isotherms of O_2 and H_2. (a & b) Fits of 2D-NLDFT models to O_2 and H_2 isotherms. (c) PSDs and pore volumes calculated from single O_2 isotherm and from both isotherms.

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S5-2

On the molecular simulation of phenol adsorption in slit-shaped carbons: role of carbon surface conductivity

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Introduction

The use of adsorbent materials is well-known as one of the most efficient ways of removing harmful molecules (micro-pollutants/pollutants). In the present contribution, the role of carbon surface conductivity on the adsorption phenomenon is studied via molecular simulations.

Material and methods

The molecular simulations of phenol adsorption in parallel conducting graphene sheets have been successfully achieved using our user-written parallel scalable GCMC algorithm (High-Performance Computing using MPI C/C++) [1-2]. The carbon surface conductivity is taken into account during GCMC simulations by introducing the analytical solution of point charge energy on an infinite conducting plane.

Results and discussion

By taking advantage of this solution, the charge distribution on the carbon surface is determined during adsorption simulation. The conductivity issue affects adsorption configuration in wide pores (1 nm) as well as so-called narrow pores (0.65 nm). It leads to more stable energy levels, greater heats of adsorption and fewer distances between phenol molecules and graphene sheet. The contribution of the different interactions among guest-guest molecules (Phenol-phenol) and guest-host molecules (Phenol and graphene sheet) are carefully investigated using parallel user-written PDF histograms, angular orientation histograms, and relevant profile densities for O-H bond in phenol molecule.

Conclusions

The simulation results of phenol in a parallel stack of graphene demonstrate that the most dominant interaction is the electrostatic interaction between the adsorbate and the adsorbent. The lack of this interaction gives the low number of adsorbed molecules, a greater distance between the adsorbent and adsorbate and even a quasi-random orientation of adsorbed molecules.

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S5-3

Kerogen texture modeling, adsorption and transport properties

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Introduction

Organic shale are an heterogeneous multiscale materials made of sedimentary rocks composed of organic mater inclusions called kerogen. These inclusions ranging from the nano to the micrometer size and are a key component in hydrocarbon production. During burial, increase of temperature (T) and pressure (P) initiate kerogen degradation, that originate hydrocarbon molecules. Molecules are trapped into the complex pore network of kerogen, ranging from subnano to the micrometer size. Physical and chemical properties of trapped hydrocarbons mixture (from 1 to few tens CHx groups) into multiscale porous system are still poorly understood.

Experimental

In order to study these systems, we have built atomistic structure of kerogen, generated from experimental data. Nanoporous kerogen was first generated by reverse Monte Carlo technique based on the neutron diffraction spectrum [1], while mesoporosity is included from tomography data of kerogen samples [2].

Results and discussion

We first evidenced by Grand Canonical Monte Carlo simulations [3] a selective or reverse selective adsorption, depending on chain lengths, pore diameters and the thermodynamical conditions of kerogen. At low T, adsorption of alkanes are favored in small pores, while at high T, adsorption of long chains are favored in large pores. These results are important about diffusion. Indeed, at small pore size, diffusion is mainly driven by the fluid/wall adsorption. Thus, depending on the thermodynamical conditions fluid diffusion follow a selective or reverse selective diffusion for small thermodynamical conditions change.

Conclusions

In this work, we connect thermodynamical behaviors to diffusion and we show the complex interplay between the kerogen texture, chemical nature of the fluid, thermodynamics and diffusion at small scale.

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S5-4

Enhanced Cyclic CO_2/N_2 Separation Performances Stability on Chemically Modified Nitrogen-doped Ordered Mesoporous Carbon

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Introduction and objectives

An ordered mesoporous carbon (OMC) prepared via soft-template method was used as support. The support surface was transformed to more hydrophilic via ammonia gas thermal treatment. After that, tetraethylenepentamine (TEPA) was introduced to obtain this solid amine sorbent. The mesoporous pore channel allowed CO_2 molecules diffusion inside easier and prevent pore blocked after functional groups and TEPA introduction compared to micropores. The properties, CO_2 capture performance, separation stability from CO_2/N_2 gas mixture under multicycle test and kinetics of this sorbent were evaluated.

Results and discussion

Characterization conducted with nitrogen adsorption/desorption isotherms, Fourier transform infrared spectroscopy, elemental analysis, and X-ray photoelectron spectroscopy demonstrated that the porosity and surface chemistry of the OMCs were tuned by the modification. Adsorption evaluation with both volumetric analysis and thermogravimetric analysis under various conditions indicated that the resulting amine introduced N-doped OMC (a-N-OMC) presented a higher CO_2 adsorption capacity with fast kinetics, outstanding selectivity at 50 °C and maintained superior separation performance after 20 cycles. The presence of accessible amino groups in considerable amounts renders the modified mesoporous carbon a promising candidate for CO_2 capture from flue gas by using the temperature swing adsorption.

Conclusions

The resulting a-N-OMC shows larger surface area and maintained mesoporosity. This sorbent presented not only enhanced CO_2 capture ability, but superior CO_2 selectivity and regeneration stability under CO_2/N_2 gas mixture. The appearance of nitrogen species on the surface retained more TEPA with well-distributed pattern inside and served as an electron donating part to stabilize TEPA molecules. These results demonstrated the great potential of a-N-OMC as CO_2 adsorbents by using the temperature swing adsorption systems.

Acknowledgements

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MoS_2@CNT hybrid for free-standing charge storage: mechanistic investigations on growth and charge storage mechanism

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Introduction

Carbon nanotube (CNT) fibers are excellent platform for the preparation of robust and free-standing electrodes for energy conversion and storage. Surface functionalization with transition metal dichalcogenides, such as MoS_2 is promisting to improve their electrochemical properties.[1,2] However, uniform functionalization of these materials, without compromising their mechanical strength is quite challenging.

Experimental

We have developed a simple strategy to uniformly cover MoS_2 on CNT fiber, that leads to a free-standing electrode. The electrodes were thoroughly characterized and used as electrodes for supercapacitor and Li-ion battery.

Results and discussion

Using a unique synthetic route, we obtained a uniform coating of MoS_2 around CNT fibers. The thickness of MoS_2 coating can be nicely manipulated by tuning the synthetic conditions. These robust MoS_2@CNT electrodes can be used in the fabrication of self-standing, flexible supercapacitor with enhanced capacitance over the pristine materials along with excellent rate capability. When used as lithium ion battery electrode, these materials have exhibited very less irreversible capacity loss, which is otherwise detrimental for such candidature. Finally, we enlighten the mechanism of charge storage capacity, which was found to undergo via intercalation, followed by a sintering process.

Conclusions

In this work, we have demonstrated that free-standing MoS_2@CNT hybrid is a promising candidate for flexible charge storage. A uniform coating of MoS_2 around CNT fibers not only improved electrochemical properties, but also improved its mechanical stability.

Acknowledgements

We acknowledge European Union and AIRBUS for funding.

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S6-2

Silicon/biogas-derived carbon nanofibers composites: a promising anode material for lithium-ion batteries

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Introduction

Silicon appears to be a promising anode material for increasing both the energy density and power of lithium-ion batteries due to, mainly, the high theoretical specific capacity, the relatively low working potential and the abundance in earth crust. However, the lithiation/delithiation of Si causes successive volume changes of this material leading to the fracture of the particles and the consequent poor reversibility and cycling stability of the electrode. Among different strategies which are being developed to avoid the Si-electrode degradation, this work has focused on: (i) the preparation of Si-based composites by adding a matrix (specifically carbon materials) which can help to buffer the volume changes and (ii) the limitation of the lower cut-off voltage (LCOV) which leads to a better control of these changes.

Results and discussion

Among different carbon matrices studied in this work, free-metal carbon nanofibers obtained from the catalytic decomposition of biogas (BCNFs) result the most suitable ones. Thus, the fishbone microstructure of these carbon nanofilaments, having a great number of active sites to interact with the Si particles, buffer the volume changes associated with the silicon lithiation/delithiation, preventing the electrode degradation. Specifically, an nSi:BCNFs 1:1 weight ratio in the active composite is the optimal. On the other hand, the limitation of the LCOV in the 80-100 mV range avoids the formation of the highest lithiated phase which leads to electrode degradation. Both strategies allow achieving a compromise between the specific capacity, which is greater than that of graphitic materials currently used in LIBs, and acceptable capacity retention along galvanostatic cycling. Thus, electrodes formed by 80 % of the nSi/BCNFs composite, including a 10 % of carbon black (CB), and 20 % of sodium carboxymethyl cellulose (NaCMC) as active material and binder, respectively, has been prepared in this work by a simple, fast and easily industrial-scaling process, achieving specific capacities up to ~ 520 mAh g-1 after 30 cycles with coulombic efficiency > 95 % and ~ 94 % of capacity retention along cycling at an electric current density of 100/200 mA g^{-1} and a LCOV of 80 mV (Fig. 1).

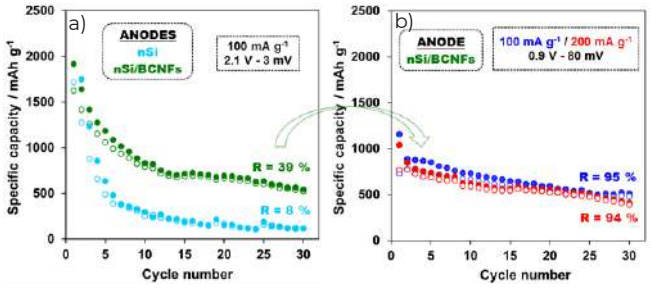

Fig. 1 Specific discharge (full circle)/charge capacity (empty circle) *vs* cycle number plots from the galvanostatic cycling of a) nSi and nSi/BCNFs composite at 100 mA g^{-1} in 2.1 V - 3mV potential range and b) nSi/BCNFs composite at 100-200 mA g^{-1} in the 0.9 V - 80 mV potential range

S6-3

Design of Hard Carbons anodes for high performance Na-ion batteries

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Introduction

Na ion batteries have attracted wide interest in the last years mainly due to the natural abundance of Na resources offering a long term valuable solution for energy storage. Hard carbons received great attention as alternative anodes for Na-ion batteries due to their disordered structure compared to graphite, which facilitates Na-ion insertion-extraction. However, the correlation between the hard carbon structure and their performances is not well understood neither the storage mechanism which is still under debate.

Experimental

Hard carbon was synthesized by heat treatment in inert atmosphere of different eco-friendly precursors (bio-polymers, polymers and waste biomass) at temperatures between 1000 and 2800°C [1-3]. Their structure, porosity and surface chemistry defects were analyzed by XRD, gas adsorption and TPD-MS. The electrochemical performances were determined vs. sodium metal using 1M solution of $NaPF_6$ in ethylene carbonate (EC)/ dimethyl carbonate (DMC).

Results and discussion

The hard carbon microstructure was found to be strongly dependent on the precursor type for a given annealing temperature. For all precursors, the increase in the pyrolysis temperature leads to a decrease in the specific surface area and surface chemistry and in an improvement of the structure (better graphitization and lower interlayer space). The electrochemical performances are in consequent dependent on the carbon characteristics and a pyrolysis between 1200 and 1400°C is optimal. The binder, additive and electrolyte used impact as well the performances as will be discussed. Therefore, capacity of around 300 mAh/g [2, 4] could be achieved for several materials along with high columbic efficiency and good cycle stability. Systematic studies were performed which allowed to correlate for the first time the capacity in the slope and plateau region with the specific surface area, interlayer distance, oxygen-functional groups and the defects [3]. For high temperature treated carbons a single plateau region could be observed for the first time in Na-ion batteries [1].

Conclusions

A balance between the carbon properties and their electrochemical formulation is required to obtain good performances in Na-ion batteries. The mechanism of Na insertion involves first, the adsorption of Na on defect sites and porosity in the slope region (high potential) and intercalation between pseudo-graphitic layers in the plateau region (low potential, < 0.1V).

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S6-4

Mesoporous Fe-C-S composites as electroactive materials for the negative electrode of an Iron-Air battery

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Introduction

Iron-air batteries (IAB) –which generate electricity from the oxidation of iron in the negative electrode and the reduction of ambient oxygen at the positive electrode– are foreseen as promising devices, due to their low cost and high specific energy, among other characteristics. The negative electrode of these batteries presents some challenges, especially related to the unwanted hydrogen evolution reaction (HER), that can be partially solved by adding sulfur-based additives [1]. Herein, we prepared mesoporous sulfur doped iron oxides and mixed them with a commercial carbon to form Fe/C composites as the electroactive material for the negative electrode of an IAB.

Experimental

Iron (II) sulfate, an organic acid (oxalic or tartaric) and sodium thiosulfate (in some cases) were precipitated and then calcined in air or nitrogen atmosphere to obtain mesoporous sulfur-doped iron oxides [2]. The materials were named Fe(acid)-S *(if they include it)* (calcination atmosphere), e.g., FeTr-S air is made with tartaric acid and sodium thiosulfate, calcined in air. The oxides were then mixed with Vulcan-XC-72R (50: 50) in a planetary mill to obtain the composites, that were tested in a 3-electrode cell, using KOH 0.1 M as electrolyte.

Results and discussion

The S-doped Fe-oxides had a surface area around 150 m^2/g and from 1.5 to 6 wt. % of S. Figure 1 shows the discharge capacities of the composites, including a commercial iron oxide. The S-doped Fe-oxides showed greater maximum discharge capacity than those without S. All the composites were more stable than the commercial Fe_2O_3 (losing 86% of its discharge capacity after four cycles versus our composites retaining up to 94%).

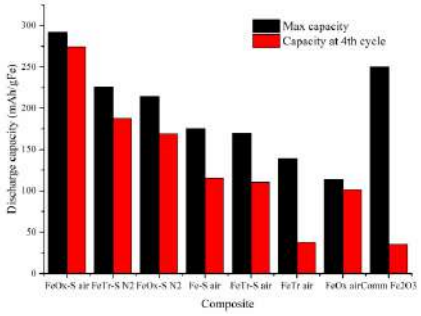

Figure 1. Discharge capacities of the different composites

Conclusions

Fe-C-S composites were obtained by a simple method and used as IAB negative electrodes with capacities up to 292 mAh/g_{Fe} and good stability, retaining a max of 94% capacity after cycling.

Acknowledgements

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S7-1

In situ X-ray photoelectron and X-ray absorption spectroscopy study of lithium interaction with fluorinated graphites

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Introduction

Owing to low weight density, high temperature stability and long shelf life, fluorinated carbons are attractive as electrode materials for primary lithium batteries. Capacitance of such battery is linked to the electrochemical reduction reaction consisting in the C–F bond breaking through LiF formation. The energy of C–F bonding is lowered with the decrease of fluorine loading. Thus, to achieve the high performance of fluorinated carbon in lithium battery, it is necessary to find optimal composition for the material. Here, we present model experiments to understand the interaction of lithium with fluorinated graphite materials. A thin layer of lithium was deposited on a surface of fluorinated flakes in preparation chamber of X-ray spectrometer, and we examined *in situ* the change in the electronic state of the elements.

Experimental

Highly oriented pyrolytic graphite (HOPG) was fluorinated using BrF_3 solution (10 vol%) in Br_2 at room temperature for 1 month. The product consisted of transparent golden colored flakes and had a composition of ~C_2F [1]. The experiments were performed using the radiation from synchrotron radiation station BESSY II. After exposure to lithium vapor from a Li-dispenser the F-HOPG flake was transferred into a measuring chamber without contact with air.

Results and discussion

A combination of XPS and angle-resolved NEXAFS data allowed detecting defluorination of sample from surface to bulk. The stoichiometry of LiF-intercalated graphite was C_2LiF. LiF nanocrystals were observed using scanning and transmission electron microscopy. NEXAFS C K-edge spectrum detected distortion of the π-cloud due to corrugation of the graphene lattice and appearance of new electronic states assigned to a charge transfer from LiF to graphene. Initial capacity of fluorinated graphene was 1770 mAh g^{-1} at a current density of 50 mA g^{-1}.

Conclusions

Li penetrates from the surface, scavenging F from the surrounding lattice to form large 3D LiF crystals, both embedded in the lattice and aggregated on the material surface, leaving zones of pristine reconstructed graphite. These results have an importance for understanding behavior of fluorinated carbons in primary and secondary battery usage.

Acknowledgements

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S7-2

Synthetic approaches for improving the electrical conductivity of mesoporous carbon gels

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Introduction

After the early works of by Pekala et al [1] on the synthesis of porous carbon gels, these materials have received great attention due to their exceptional properties, such as mechanical and chemical stability, high specific surface area and tuned morphology. Particularly, special attention has been paid to the improvement of the electrical conductivity of carbon gels [2]. In this regard, our previous studies showed that the incorporation of carbon black as a conductive additive does not only impact the electronic properties of the carbon gel, but it also has a strong impact on the development of the porosity [2]. Bearing this in mind, in this study we have investigated the effect of the nature and amount of various carbon additives (e.g., graphite, carbon black, graphene derivatives) in the porosity of the final carbon gels.

Experimental

The synthesis of the carbon gels was carried out following a simple modification of the traditional sol-gel method, as reported elsewhere [1]. Briefly, the polymerization of resorcinol and formaldehyde mixtures is carried out in an aqueous medium using a sodium carbonate as catalyst, and various amounts of additives (ranging between 5-50 wt. %) of different physicochemical properties. The mixtures were stirred, sealed into glass moulds at 70 ºC for 4 h to promote the gelation and ageing, and then dried at 150 °C for 12 h. The wet gels pyrolysed under inert atmosphere and characterized using complementary techniques.

Results, Discussion and Conclusions

A series of carbon nanostructures with different composition were selected as additives for the preparation of the carbon gels with improved electrical conductivity: graphite, graphene oxide, carbon black. Due to the hydrophobicity of most of the studied additives, an optimization of the sol-gel process was initially performed (co-solvents, mechanical stirring) to assure the dispersion of the additives during the polycondensation of the precursors to form the wet gels. The characterization of the obtained carbon bels showed that the presence of the additive has a strong impact on the fraction of large pores. The resulting materials displayed a multimodal mesoporosity, which volume fraction was highly dependent on the amount of additive incorporated. Data suggested that the morphology of the additive controls its location in the final carbon materials, thereby impacting the conductivity.

Acknowledgements

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S7-3

Synthesis and characterization of graphene-related nanomaterials by catalytic chemical vapor deposition using a Co-Cu/Cellulose-Derived Carbon catalyst

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Introduction

Large-scale production of emerging carbonaceous nanomaterial (CNMs) requires the design and optimization of new types of multifunctional catalysts. This work presents the selective synthesis of carbon nanotubes (CNTs) via catalytic chemical vapor deposition (CCVD) of methane over a Co-Cu/carbon catalyst derived from cellulose (CDC).

Experimental

The catalysts were prepared by thermal decomposition, under reductive atmosphere, of cellulose previously impregnated with the metallic precursors [1]. The reaction was carried out at atmospheric pressure in a thermobalance operated as a differential reactor.

Results and discussion

The evolution along time of carbon content indicates that the productivity obtained is maximum at 800 ºC (see Fig. 1a), reaching a value of 0.3 g_C/g_{cat}·h. TEM images show that the growth of CNTs occurs at temperatures below 850 ºC (see Fig. 1b). In contrast, graphitic nanolayers surrounding the metallic nanoparticles are formed at higher temperatures.

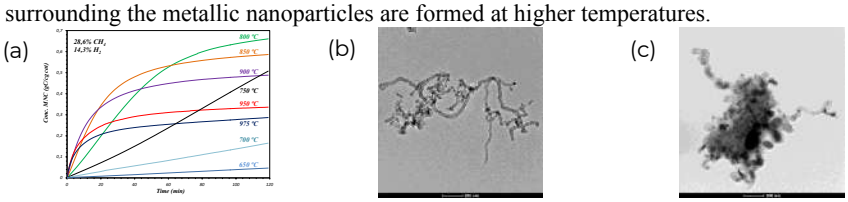

Fig 1. (a) Mass carbon vs. time. (b) TEM image after CCVD reaction at 750 ºC and (c) 950 ºC.

Conclusions

Co-Cu/CDC catalyst is suitable material for the production of CNTs by CCVD of CH_4. The characterization results indicate the CNTs growth is favored at temperatures below 850 ºC.

Acknowledgements

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S7-4

Carbon microtubes derived from self-rolled chitosan acetate films and graphitized by joule heating

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Introduction

Carbonized micro- and nanostructures, derived from polymer precursors, have gained in the last years considerable interest. We propose a fast and efficient approach for fabrication of carbon microtubes with graphitic structure by combining the self-rolling of chitosan films, carbonization, and joule heating [1].

Experimental

Chitosan films, prepared by casting technique on glass slides, were thermally treated at 150°C for 3 min. In water the films spontaneously rolled up forming the tubes of submillimeter diameter Dried tubes were carbonized at 900°C, and then heated by the joule effect at 2500°C.

Results and discussion

Local temperatures as high as 2500°C and high graphitization degree, confirmed by Raman spectroscopy and TEM can be easily reached due to the joule heating effect.

Conclusions

The graphitic microtubes can be explored as CVD microreactors, enabling very rapid heating and cooling kinetics, due to their small dimensions and very effective radiative cooling at high temperatures.

Acknowledgements

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S8-1

Biomass upgrading via H_2-free HDO using highly effective carbon-based catalysts

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Introduction

Nowadays, the production of hydrocarbon fuels from biomass is a major challenge in the effort to develop advanced biofuels for a sustainable future. The removing of the oxygen atoms from the produced bio-oils is needed and catalytic hydrodeoxygenation (HDO) reaction is a promising route. However, this reaction requires the supply of H_2, limiting the economic viability of their implementation in large scale production units [1]. In this work we propose to use water as hydrogen source, thus reducing the costs of the bio-oil upgrading process. As model reaction, hydrogen free guaiacol hydrodeoxygenation was investigated using different noble metal (Ru, Rh, Pd, Au)-carbon based catalysts.

Experimental

A charcoal powder DARCO® was used as carbon support. Catalysts were prepared by wetness impregnation with acetone and aqueous solutions of metal precursors. Gold catalyst was prepared by colloidal synthesis. In all cases, 2% (wt.%) of the reduced metal was used.

The HDO catalytic activity was tested in a Parr reactor at 50 bar pressure and 250°C during 4 h. 50 mL of a 0,01 mg/mL guaiacol solution and 200 mg of catalyst was used. Guaiacol and possible products were determined by gas chromatography with a flame ionisation detector.

Results and discussion

All catalysts present noble metal particle sizes below 7 nm. They are slightly acidic and the metal dispersion decreased in following order: Ru/C>Pd/C>Au/C>Rh/C.

All the catalysts are active in the process, Ru/C being the most promising material (25% guaicol conversion), in good agreement with the metallic dispersion trend. This sample is rather selective to partial de-oxygenated products and seems to promote demethoxylation and dehydroxylation reactions. More interestingly, this sample is stable showing a very slight activity drop after three reaction cycles, with no metallic sintering

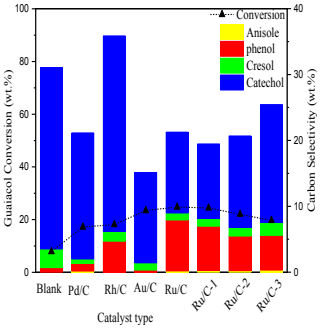

Figure 1. HDO conversion

Conclusions

"H_2 free" HDO reactions using noble metal based catalysts is a viable process and could a significant impact in biomass upgrading technologies.

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S8-2

Production of hydrocarbons by hydrodechlorination using functionalized carbon nanofibers

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Introduction

Methane, the main component of natural gas, is also obtained from waste refinery or renewable sources like bio-refinery. In this work, a method for the valorization of methane is proposed, exploring the hydrodechlorination (HDC) of chloromethanes (obtained from methane chlorination) as an alternative process for the production of valuable hydrocarbons for industry, such as olefins or paraffinic hydrocarbons heavier than methane.

Experimental

Commercial carbon nanofibers (CNF) have been functionalized by: (i) oxidation with HNO_3, (ii) treatment with HCl, and (iii) physical mixture with urea. These solids have been used as supports for the synthesis of 1 wt.% Pd/CNF catalysts, which have been tested in the HDC of chloroform (TCM), using an inlet TCM concentration of 1000 ppm, a H_2/TCM molar ratio of 50, a space-time of 0.2 kg h mol^{-1} and reaction temperatures between 150 and 250 °C.

Results and discussion

All the catalysts showed increasing conversion with reaction temperature in the HDC of TCM, removing *ca.* 40, 50, 60 and 70% of TCM with Pd/CNF-Urea, Pd/CNF-HCl, Pd/CNF-HNO_3 and Pd/CNF respectively, at 250 °C. The same trend was observed when analyzing the palladium particles size by TEM, showing Pd/CNF-Urea the smallest particles (mean size 1.7 nm), and Pd/CNF the highest (3.8 nm), pointing to the relation between these two properties. In all the cases, the production of chlorinated byproducts was negligible. Methane was the main reaction product found for all the catalysts at the lowest temperature tested. However, selectivity to valuable hydrocarbons (C2-C3) always increased with reaction temperature, being remarkable the high selectivity to olefins found for Pd/CNF-Urea at the highest temperature tested (57%) in comparison with methane and light paraffins (43%). The surface proportion of Pd^{n+} in the catalysts seems to be determinant in the selectivity of the process.

Conclusions

All catalysts show high initial activity in the HDC of TCM, finding a direct relation between Pd particles size and TCM conversion. Selectivity to light olefins is favored by increasing the reaction temperature. The Pd^{n+}/Pd^0 ratio in the catalysts influences the process selectivity.

Acknowledgements

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S8-3

Ru, Pd, Pt as dopants of carbon nanofibers-supported Ni catalysts for one-pot cellobiose conversion

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Introduction

The reduction of sugars to their hydrogenated forms (sorbitol) emerges as an effective chemical route for enhancing the productivity of cellulose depolymerization process [1]. Whereas nickel does not fulfill the activity and selectivity criteria at low metal contents, its doping with noble metals could represent an economical trade-off.

Experimental

A series of carbon nanofibers (CNF) supported Ni-noble metal (Ru, Pt, Pd) catalysts, with intended metal loadings of 3.0 and 0.5 wt.%, respectively, was prepared by wet co-impregnation of the precursor salts, followed by thermal decomposition and H_2-reduction. The samples were characterized by different techniques (ICP-OES, XRD, TPR and HRTEM) and tested in the hydrolytic hydrogenation of cellobiose (180ºC, 4.0 MPa of H_2, 3h).

Results and discussion

The Ni-noble metal alloy formation induced changes on the size and dispersion of the Ni phase and favored its reductive properties, which was translated into an enhancement on the catalytic performance. A remarkable synergic effect was noticed for Ni-Pt/CNF and Ni-Pd/CNF, since the yield of hydrogenated products (96.0 and 61.2 %, respectively) exceeded the sum of the activity of their pure constituents separately (32.9, 0.44 and 25.9 % for Ni/CNF, Pd/CNF and Pt/CNF) (Figure 1). In turn, Ru/CNF enabled the practically total hydrogenation of cellobiose, making unnecessary the Ni-Ru alloy formation.

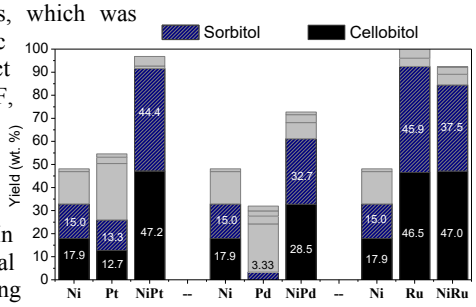

Figure 1. *Summarized catalytic results*

Conclusions

The Ni selectivity towards targeted compounds was enhanced upon alloying it with Pt, Pd and Ru. TPR-H_2 results and the analysis of the morphology of the metal particles helped to understand the origin of this improved catalytic behavior.

Acknowledgements

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S8-4

Noble metals supported on mesoporous biochar as a suitable catalyst for upgrading bio oils

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Introduction

The production of hydrocarbon fuels from biomass is a major challenge in order to produce new biofuels, and the thermolysis of lignocellulosic biomass has attracted attention in the last decade and appears to be a practical method to produce bio-oils. However, the oxygen atoms in bio-oils must be removed, and the catalytic hydrodeoxygenation (HDO) reaction becomes an interesting approach. In this work, we evaluate the effect of the nature of the noble metal (Pd, Ru, Au) supported on mesoporous biochars on the catalytic activity towards the aqueous phase HDO of vanillin, a model molecule of biomass derived feedstock [1].

Experimental

Biochars obtained from pyrolysis of vine shoot and microcrystalline cellulose was used as support. Different chemical ($ZnCl_2$, HNO_3) and physical (CO_2) activation treatments were carried out in order to produce support with different textural properties. Pd and Ru catalysts were prepared by wetness impregnation and Au-samples were synthesized by the colloidal route. In all cases, the catalysts were synthetized with a nominal noble metal content of 2 wt.%. All solids (fresh and reacted) were fully characterized and the HDO catalytic activity was tested in a Parr reactor at 30 bars and 100°C during 3 h, with a 100 mL of a 1mg/mL vanillin solution and 50 mg of catalyst.

Results and discussion

All catalysts present an average noble metal particle size below 10 nm. After 3 hours' reaction, vanillin was completely consumed for Ru and Pd catalysts. The highest selectivity to p-creosol, 92%, was obtained with the Pd/C system. It is demonstrated a positive influence of the chemical treatment of the raw biomass in the final characteristics (mesoporosity) and catalytic activity of the systems. Besides this, hydrodeoxygenation activity increased with increasing metal dispersion. A kinetic model including adsorption of vanillin is developed to describe all the experimental data obtained

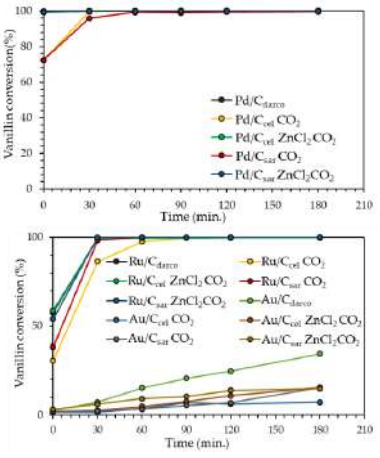

Figure 1. Vanillin conversion

Conclusions

Effective catalytic HDO of vanillin to p-creosol under mild reaction conditions has been carried out using noble metal nanoparticles supported on mesoporous biochars. Palladium is shown to be the most active and selective metal.

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S8-5

Templated carbons for the study of the influence of morphology, porous texture and N-doping of catalytic supports in aqueous-phase hydrodechlorination

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Introduction

Carbon materials are well known and deeply studied as supports in heterogeneous catalysts because of their interesting and modifiable characteristics influencing catalytic performance, such as morphology, texture and surface chemistry, including the presence of heteroatoms.

Experimental

Morphology/texture of carbons were controlled by templating with MSU-F, SBA-15 and silica spheres, obtaining mesocellular, CMK-3 type and submicro hollow-spherical carbons, respectively, after pyrolysis of infiltrated resol resin and template removal. 1,10-phenantroline was used as N dopant. Pd (incipient wetness impregnation, IWI) or Pt (IWI and in-situ colloidal synthesis) were supported on the carbons and tested in 4-chlorophenol hydrodechlorination.

Results and discussion

The observed influence of doping is different among the three materials studied but in general terms, increasing catalytic performance with a negligible effect on texture. For mesocellular carbons an increase of activity and decrease of Ea was observed with total selectivity to phenol, while other products were detected in noticeable concentrations when CMK-3 type and submicrosphers were used (cyclohexanol and cyclohexanone, respectively). Pd catalysts increased their activity at low temperature (30-60ºC), although their selectivity to hydrogenation products was affected by the used as support; phenol as the only product detected using mesocellular supports. The morphology and high mesoporosity ot these materials contributed to a high activity due to negligible mass transfer constrains. IWI Pt catalysts supported on N-doped CMK-3 increase the activity with T (70ºC), due to the influence of doping in NP formation, showing, in addition, with very high selectivity to cyclohexanone.

Conclusions

N-doping of carbon supports influenced the activity of catalysts in a different way depending on the metal and support. Supports led to Pd catalysts with higher activity at low temperature than non-doped, whereas for Pt an activity boost was observed for doped supports at high T.

Acknowledgements

AEI/MINECO grant CTQ2012-32821 and C. Ruiz-García PhD grant BES-2013-06608.

S8-6

H_2 production on 1D and 2D Carbon-containing Fe-, Co-, and Ni-based foamy catalysts

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Introduction

One of the most important goals in the XXI consists of developing sustainable processes to produce clean energy. On the other hand, due to the increasingly marked effect of global warming, it is necessary to implement or improve old chemical processes that involve capturing and converting CO_2, such as dry methane reforming (DMR). Our group have reported [1] some interesting results for DMR to produce selectively hydrogen using activated-carbon Ni-based catalysts. Now, a novel approach concerns with the development of noble-metal free catalysts supported on graphene-like foams. Thus, the objective of this work is to show a single methodology to prepare graphene-like foams Fe, Co- and Ni-based catalysts for the production of hydrogen by DMR and related reactions.

Experimental

The synthesis of 2D and 3D porous carbon-based materials were performed from the controlled pyrolysis of saccharose in the absence [2] or presence of KOH [3]. A thorough characterization was performed by gas adsorption, XRD, XPS, SEM, TEM, NEXAFS and RAMAN. The catalytic assays of DMR were performed at atmospheric pressure in a continuous-flow reactor as reported elsewhere [1], and the methane conversion and hydrogen production was followed by GC.

Results, Discussion and Conclusions

XRD showed that graphite is the main crystalline phase of the prepared samples, although XPS revealed important differences with respect to graphite. NEXAFS and RAMAN spectroscopy suggested the formation of graphene oxide. The textural analysis pointed out a hierarchically pore structure in the graphene-based materials. Regarding catalytic activity, Fe-, Co- and Ni-doped carbon foams are clearly more active and suffer less deactivation than bulk conventional catalysts prepared by wetness impregnation. It can be concluded then that the controlled pyrolysis of saccharides opens a low cost and eco-friendly method for the preparation of graphene-based catalytic membranes and membrane reactors prepared from the polysaccharide fraction of biomass wastes.

Acknowledgements

The authors thank the financial support of: Franco-Chilean network BIOCval2E (REDES-170004), CONICYT PIA/APOYO CCTE AFB170007, CONICYT-FONDECYT project 1190591, and Millennium Science Initiative (Chile)-Nuclei on Catalytic Processes towards Sustainable Chemistry.

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S8-7

N-doping of carbon support for creation of efficient catalysts for hydrogen production from formic acid decomposition

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Introduction

Carbon nanomaterials are widely used as supports for metallic catalysts. Weak interaction of these supports with a metal-catalyst can lead to metal sintering providing a decrease of the catalytic reaction rate. In this presentation, we will show that sintering of metal could be diminished by N-doping of the carbon support. Some N-sites incorporated into the carbon strongly interact with metal atoms providing high stability and activity of the catalyst in hydrogen production from formic acid (HCOOH) which could be produced from biomass.[1]

Experimental

N-free and N-doped carbon supports were prepared by CVD from ethanol or acetonitrile, respectively, at 1073 K. The N-doped carbon contained 6 wt% of nitrogen. After deposition of metal salts, the samples were reduced in H_2 or HCOOH at 573 K. The catalytic reaction was performed in a 2% HCOOH/He flow.

Results and discussion

A HAADF/STEM study showed that Cu was present as nanoparticles (~35 nm) in the N-free Cu/C catalyst after the reaction. In contrast, it was present as clusters (~5 nm) and single atoms in the N-doped Cu/N-C catalyst (Fig. 1). According to XPS data and DFT calculations, stabilization of highly dispersed Cu in this catalyst takes place owing to its coordination to pyridinic N sites. The high Cu dispersion allows reaching a higher rate of H_2 production from decomposition of HCOOH as compared to the N-free catalyst.[2]

Deposition of Pt or Pd on the N-doped carbon also leads to stabilization of metals in the atomic state and in the state of clusters (~1 nm for Pt, ~2.5 nm for Pd). XPS data indicated that after the reduction of the samples in the spectrometer at 573 K, a significant ratio of Pd is still present in an oxidized state assigned to single Pd ions attached to pyridinic N species. These single ions are stable in the reaction and can react with HCOOH with a higher rate than the rate provided by the surface atoms of nanoparticles. This was confirmed by our DFT calculations.[3]

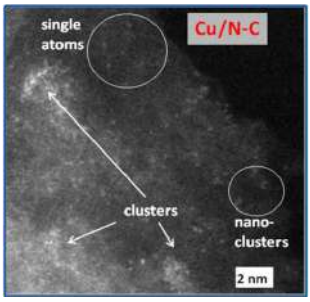

Fig. 1 HAADF/STEM image of the 4.5 wt% Cu/N-C catalyst.

Conclusions

N-doping of carbon supports opens new possibilities in catalysis due to efficient utilization of metal in a highly dispersed state, high reaction rate, selectivity and stability.

Acknowledgements

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S9-1

Synthesis of hierarchical TiO_2/MWCNT photocatalysts for VOCs abatement

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Introduction

The elimination of volatile organic compounds (VOCs) at low concentration is a subject of great interest. Carbon nanotube- titanium dioxide (CNT-TiO_2) composite systems are currently one alternative towards the total abatement of VOCs due to its advantages as for example a large specific surface area and an increase of the lifetime of electron-hole pairs.[1]

Experimental

TiO_2/MWCNT materials were synthesized by incorporating 1wt% MWCNT (TiO_2/MWCNT_UB_5min and TiO_2/MWCNT_UB_1h; MWCNTs were dispersed for 5 min and 1 h using an ultrasonic bath, respectively. TiO_2/MWCNT_UP_5min; MWCNTs were dispersed for 5 min with an ultrasound probe) during the synthesis of TiO_2.[2] The materials synthesized were characterized (UV, TEM, TG and active surface area (ASA)). The photocatalysis experiments were carried in the conditions of TiO_2 analyzed in a previous work.[2]

Results and discussion

TEM and ASA analysis show that the sample dispersed with an ultrasound probe (TiO_2/MWCNT_UP_5min) presents a better dispersion and more defects in the MWCNT with respect to the other composites (Figure 1 and Table 1). Moreover, the modified properties of the MWCNT in the composites can change the photocatalytic performance of these materials as shown in Table 1, where TiO_2/MWCNT_UP_5min can remove almost 90% of propene.

Figure 1. TEM of the samples used in this study

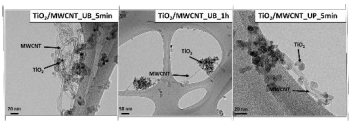

Table 1. ASA characterization and conversion of propene for TiO_2/MWCNT samples and TiO_2

Sample	ASA MWCNT (m^2/g)	% Propene Conversion
TiO_2/MWCNT_UB_5min	8.7	75
TiO_2/MWCNT_UB_1h	9	74
TiO_2/MWCNT_UP_5min	12	87
TiO_2	-	65

Conclusions

The composite with efficient dispersion and a high number of defects in the MWCNT during synthesis presents high propene conversion under flow conditions in gas phase.

Acknowledgements

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S9-2

Photocatalytic activity of semiconductor-free, tannin-derived mesostructured carbons

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Introduction

Ordered mesoporous carbons (OMCs) are of great interest in various areas for the so-called XXI century's sustainable society. Energy production/storage and environmental remediation are two of the main applications of these materials [1,2]. The objective of the present work was to prepare OMCs by a sustainable and eco-friendly methodology and to verify the influence of their surface chemistry and pore size distribution upon the uptake of Rhodamine B (RhB) and its photocatalytic degradation.

Experimental

Ordered mesoporous carbons (OMCs) were prepared using mimosa tannin (T) as carbon precursor and the triblock copolymer Pluronic F127 (P) as micelle generator. After carbonization of the T-P mesophase, an OMC was obtained and labeled C1, and activated with CO_2 at 850°C for 0.5, 1, or 2 h. The resultant activated OMCs (AOMCs) were labeled C1-0.5h, C1-1h and C1-2h, respectively. Samples were characterized by gas adsorption. The uptake of RhB was studied and Langmuir and Freundlich parameters were obtained. Photocatalytic tests were performed under solar irradiation and kinetic results were correlated with the adsorption parameters.

Results and discussion

An increase in the BET area (A_{BET}) was found with the activation time, as a consequence of the increase of the micropore volume. A_{BET} ranged from 780 to 1090 $m^2\ g^{-1}$. The total volume of pores increased from 0.59 up to 0.82 $cm^3\ g^{-1}$ after 2 h activation, while the mesoporous contribution to the total pore volume has a minor decrease, from 57% down to 49% after 2h of activation. All activated samples showed an increased photocatalytic activity, suggesting that the increase of the micropore volume together with the formation of reactive oxygen species [3] are responsible of their photochemical activity. C1-0.5h and C1-1h showed similar activities than TiO_2-P25, while the C1-2h had up to 3.4 times higher photoactivity than TiO_2.

Conclusions

The increase of the micropore volume together with the higher oxygen content on the surface produced by CO_2 activation enhanced the photocatalytic activity of the activated ordered mesoporous carbons under solar irradiation.

Acknowledgements

J. Matos acknowledges the Chilean projects: CONICYT-FONDECYT 1190591, CONICYT PIA/APOYO CCTE AFB170007, and the Millennium Science Initiative from Chile, grant Nuclei on Catalytic Processes towards Sustainable Chemistry (CSC). This study was partly supported by TALiSMAN project, funded by FEDER (2019-000214).

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S9-3

Application of pulsed laser deposition for fabrication of carbon cloth-based free-standing bifunctional electrodes for water splitting

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Introduction

Currently, the large scale application of water electrolysis is limited by the high cost of the noble metal-based electrocatalysts of both hydrogen (HER) and oxygen evolution reactions (OER). Recently, the carbon-based materials and their composites are emerging as their cheaper and more abundant alternatives. Pulsed laser deposition (PLD) is a technique of thin film deposition, which ensures good repeatability of the deposition process as well as precise control over the growth parameters.[1]

Experimental

The cobalt-based films were deposited on the electrochemically activated carbon cloth (EACC) by means of PLD, applying KrF excimer laser (UV, λ = 248 nm) for ablation of pure cobalt target with a pulse energy of 180 mJ. Oxygen with pressure of 75 mTorr was used as background gas. The experiment was performed at different substrate temperatures during deposition (25, 100, 200, 300, 400°C). The materials were characterized in terms of morphology, and surface structure and composition and their electrocatalytic activity in HER and OER was evaluated by linear sweep voltammetry and chronopotentiometry techniques in 1 M KOH.

Results and discussion

The X-ray photoelectron spectra and Raman spectra indicate that the main component of the films prepared at the temperatures up to 200°C was $CoCO_3$, while at the higher temperatures the films were composed of mostly composed of Co_3O_4 with crystallinity increasing with increasing deposition temperature. The scanning and transmission electron microscopy images show that the deposition temperature affected strongly the surface morphology of the deposited films.

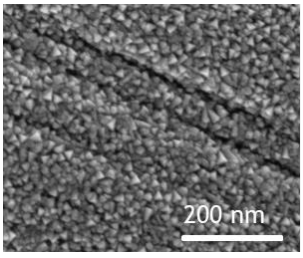

Figure 1 *SEM image of the Co_3O_4 film deposited at the temperature of 300°C.*

Conclusions

The results show that the morphology of the deposited films has a crucial influence on the electrocatalytic activity of the deposited films. The electrodes with Co_3O_4 films prepared at 300°C possess the highest electrocatalytic activity in both HER and OER, due to the biggest electrochemically active surface area with active edge sites, created by pyramid-like monocrystalline domains.

Acknowledgements

The work was supported by the statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wrocław University of Science and Technology and from the EU-H2020 research and innovation programme under grant agreement No 654390 having benefitted for the access provided by ICN2 in Barcelona within the framework of the NFFA-Europe staff members Transnational Access Activity.

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S9-4

Electrospinning of Alcell lignin for the preparation of ORR electrocatalysts

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Introduction

Carbon fibers are one of the components of the electrode assemblies used in fuel cells. They are usually prepared from polyacrylonitrile, a non-renewable synthetic polymer. Lignin is a highly abundant biopolymer that is obtained in large amounts as a byproduct in the papermaking and biofuel industries. It can be used as renewable precursor in the production of carbon fibers. In this sense, we have reported the production of carbon microfibers by coaxial electrospinning of Alcell lignin [1]. It is also possible to load platinum on these fibers, obtaining excellent catalysts for methanol oxidation [2]. In this work we report the production of electrocatalysts for the oxygen reduction reaction (ORR) via electrospinning of Alcell lignin/metallic salt solutions, enabling the replacement of synthetic polymers as raw material.

Experimental

Different metallic salts have been added to 1:1 lignin:ethanol solution and electrospun using a coaxial spinneret. Metal loaded carbon mats of different loadings have been obtained after the thermostabilization and carbonization of the electrospun fibers. The ORR activity of these samples has been studied using rotatory ring-disk electrode in 0.1 M KOH saturated with O_2.

Results and discussion

STEM-EDX images on Figure 1 shows that carbon fibers with loadings between 5 and 15 % of well-dispersed metal nanoparticles are successfully obtained through the proposed method. N_2 adsorption measurements reveals the development of wide mesopores during the carbonization process. These samples have outstanding ORR electroactivity, having water selectivity and onset potentials similar to commercial Pt-C catalysts, but using lower loadings.

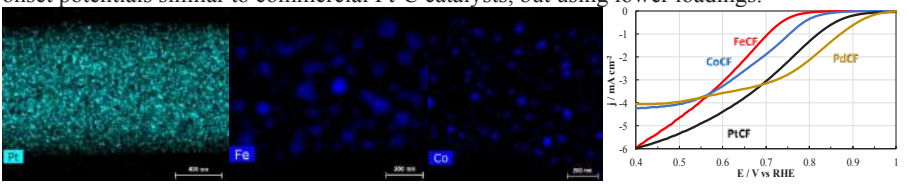

Figure 1. EDX mapping of different metal-loaded CFs, and LSV-ORR activity in 0.1M KOH

Conclusions

Synthesis of carbon fibers with supported metallic nanoparticles have been obtained by electrospinning of lignin/metallic salt solutions. The resulting carbon mats shows an excellent performance, confirming that these carbon mats are promising ORR catalysts.

Acknowledgements

The authors acknowledge the support by MINECO/FEDER (CTQ2015-68654-R and PTA2015-11464-I) and MICINN (RTI2018-097555-B-100).

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S9-5

In-situ formation of active C-O-Fe species during the water splitting process

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Introduction

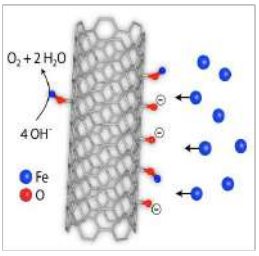
Carbon materials have been widely used as electrodes. However, due to the complexity of the carbon surface chemistry and the dynamic changes of the carbon surface during reactions, the understanding of the role of carbon in different applications is mainly driven by a trial-and-error approach. Determining the evolution of the carbon surface in different applications is essential for understanding the mechanism and design of appropriate knowledge-based electrodes. It is a big challenge to characterize the carbon surfaces in detail under real active conditions, since carbon materials hydrolyze in water and even more easily in alkaline or acidic electrolytes. In addition, electrolytic water oxidation takes place at applied potentials, which can lead to deviations between the actual and measured structures if these are not carried out in-operando.

Results and discussion

Highly graphitic carbon nanotubes (CNTs) were applied as anode material for water oxidation and by varying the surface properties of functional groups a good reaction rate can be reached.[1] By the analysis of carbon surface oxygen functional groups,[2] we illustrate the development of the functional groups during the reaction. Although carbon itself does not provide the direct active sites for water oxidation, the phenol and carbonyl groups on the carbon surface are indispensable for the dynamic formation of the real active C-O-Fe site with the trace iron impurities of the electrolyte.

Conclusions

We disclosed the dynamic change of the carbon surface chemistry during the electrocatalytic process and confirmed that specific oxygen functional groups on carbon surface play an important role for the water oxidation. These functional groups can in-situ react with iron impurities from the electrolyte forming C-O-Fe as intrinsic active sites for the reaction, which also protects the carbon surface from deep oxidation. Although carbon itself can be oxidized at oxidative potential, the special combination of functional groups and iron makes carbon-based materials a suitable anode material for water electrolysis.



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S9-6

TiO_2-C materials prepared by hydrothermal synthesis for their application in photocatalysis

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Introduction

There is a growing interest in developing more efficient TiO_2 photocatalysts, being the incorporation of carbon an interesting option [1]. Thus, preparation of TiO_2-C materials by hydrothermal (HT) synthesis with saccharose (SAC) as C precursor has been studied. It is an inexpensive low temperature one-step method that avoids surfactants and uses an abundant C precursor. The concentration of the HCl solution, used as hydrolysis agent, and the temperature of the post-synthesis treatment are the variables of the study. Comparison with an analogous series of samples prepared without carbon [2] is included.

Experimental

4 ml TTIP were added to 1.25 g SAC dispersed in ethanol (20 ml). The mixture was stirred (1 h) and ultrasounds treated (30 min) and, then, a solution containing HCl of variable concentration (0.5-12 M, 4 ml) and ethanol (10 ml) was added dropwise, followed by 1 h stirring. Afterwards, it was transferred to a 50 ml Teflon-lined stainless-steel autoclave (180 °C, 12 h). The resulting solid was filtered, dried (100 °C, 12 h) and heat-treated (air, 5 °C/min up to 350 °C, 2 h). The photocatalysts were characterized (N_2 adsorption, TG, XRD, XPS and UV-vis) and tested in the gas phase photo-oxidation of propene (100 ppmv in synthetic air, UV-lamp of 365 nm peak (TL 8W/05 FAM, Philips), being the outlet gas analyzed by mass spectrometry.

Results and discussion

The carbon content after the HT synthesis is 30 wt. %, but it strongly decreases upon the post-synthesis heat treatment, up to 0.34-0.39 wt. %. From XPS data C seems to be incorporated into the TiO_2 lattice. Anatase (70-79 %) is the only crystalline phase, in contrast to bare TiO_2 materials that contain mixed phases (with 50-69 % anatase), showing both series of samples similar textural properties. TiO_2-C photocatalysts show higher propene conversion than the analogous bare TiO_2 samples or commercial P25 titania, being the best-performing ones those prepared with 0.5 and 0.8 M HCl and heat treated at 300 ºC. In these conditions, a suitable combination of good textural properties and high anatase content is obtained.

Conclusions

TiO_2-C photocatalysts were prepared by hydrothermal synthesis in mild conditions. They contain only anatase in high proportion and their textural properties are similar to those of analogous TiO_2 samples. They are more active for propene oxidation than bare TiO_2 samples and TiO_2-P25, likely as a result of their textural properties and high anatase content.

Acknowledgements

The authors thank MICINN and FEDER (RTI2018-095291-B-I00), GV/FEDER (PROMETEO/2018/076) and University of Alicante (VIGROB-136) for financial support.

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S10-1

Superactivated carbons synthetized by steam activation of acid-chars for pharmaceuticals removal

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Introduction

Acid-mediated carbonization (AMC) is a promising route to convert carbohydrates and biomass residues into acid-chars that are excellent precursors for the synthesis of superactivated carbons[1]. In the present work, sisal residues and glucose were used as precursors for the synthesis of acid-chars (H_2SO_4 catalyst) which were further steam activated.

Experimental

Superactivated carbons were prepared from sisal (S) rejects of rope industry and glucose (G), through a two-step methodology. Firstly the precursor was digested (15 min at 50 ºC) with H_2SO_4 (9, 12 and 13.5 M) followed by a polycondensation reaction (6h at 90 ºC) after what the obtained solid (acid-char) was washed, dried, milled and sieved (< 0.148 mm)[2]. For the steam activation 1 g of the acid-char was treated during 1 h at 850-925 ºC in a N_2 flow (5 cm^3/s) with water vapor provided by a bath at 70 ºC. Materials were characterized by SEM, N_2 adsorption at -196 ºC, elemental analysis, ash content, pH at the point of zero charge (pH_{PZC}) and apparent density. Selected samples were assayed as adsorbents for two pharmaceuticals from aqueous solution (kinetics: 6 mg carbon/30 cm^3 of ibuprofen or iopamidol 180 mg dm^{-3}).

Results and discussion

Superactivated carbons with BET areas up to 1987 m^2/g and slightly acidic surfaces were obtained, regardless H_2SO_4 concentration used in AMC. Acid-chars prepared with 9 M H_2SO_4 originated materials with mesopore volumes accounting for 20% (S) and 31% (G) of the total pore volume, while higher H_2SO_4 concentrations yielded exclusively microporous samples (Figure 1).

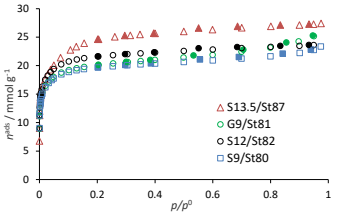

Fig. 1. N_2 adsorption isotherms of the materials.

Conclusions

The steam activated acid-chars outperformed a commercial golden standard for ibuprofen and iopamidol removal from aqueous solution, and compete with those obtained by KOH or K_2CO_3 activation of sisal acid-chars with the advantage of being prepared by a more economic and environmental friendly synthetic route.

Acknowledgements

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S10-2

Development of Ni catalysts supported on Cellulose Derived Carbon for CO_2 Methanation

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Introduction

The CO_2 use as a raw material to produce renewable fuels is a very useful route to decrease atmospheric CO_2. In this work, we present the results of hydrogenation of CO_2 to methane using Ni based catalysts supported on carbon derived from cellulose (CDC), synthesized by mineralization techniques [2].

Experimental

The catalysts were prepared by incipient wetness of the cellulose with the metallic aqueous solution (3,5%Ni; Ni/Mg/Ce=1/1/0, 1/0,5/0,5 and 1/0/1). After, thermal decomposition conditions used were: heating rate=50ºC/min, T_{max}=600ºC, t=3h. Catalytic test conditions were: m_{cat}=0,1g, GHSV=7,4·10^4 h^{-1}, H_2/CO_2=4/1.

Results and discussion

TEM and XRD characterization shows that the catalysts prepared are formed by nanoparticles (NPs) (5-16nm) of Ni, MgO and/or CeO_2, which are well dispersed on carbonaceous support. Moreover, N_2 adsorption results indicate that the substitution of Mg for Ce produces an increase of the specific area but also a progressive decrease in the pore volume, reaching 360m^2/g and 0,179cm^3/g in the case of NiCe/CDC catalyst. Activity results show that the addition of Mg and Ce to the catalyst (NiMgCe/CDC) improves the activity (X_{CO2}=71%) and selective to CH_4 (97%), reaching the highest yield to CH_4 (Y_{CH4}=69%) at 350ºC (Figure 1 left). The stability tests of the catalysts at 350ºC (Figure 1 right) show that this catalyst is also the most stable. XRD results indicate that the deactivation process is caused by the sinterization of the Ni NPs.

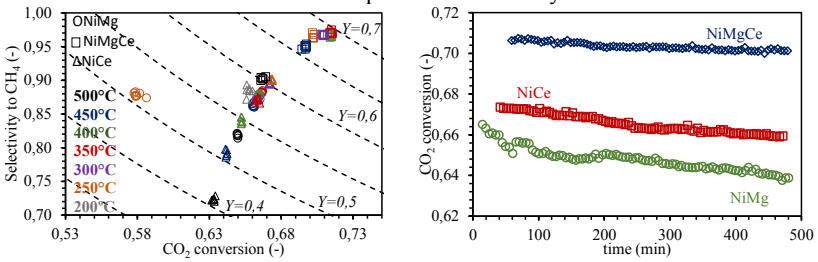

Figure 1. S_{CH4} vs. X_{CO2} at different reaction temperatures (left) and evolution of X_{CO2} vs. time at 325ºC during 8h (right).

Conclusions

The catalysts obtained by mineralization technique show good textural properties with nanoparticles well dispersed on the carbonaceous support. These catalysts are very active in the hydrogenation of CO_2. NiMgCe/CDC shows the best yield due to its high activity and selectivity. In addition, this catalyst presents a very stable activity during 8h, while NiMg/CDC and NiCe/CDC are deactivated due to a sintering process of the Ni NPs.

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S10-3

Effect of multi-scale texture of activated carbons and ultrasound treatment on the adsorption of carbamazepine and ibuprofen in water

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Introduction

Adsorption kinetics of organic micropollutants are very quick on powder but controlled by diffusion on materials having a multi-scale porosity (microscopic and mesoscopic). This implies long time length (few days and sometimes weeks) to attain adsorption equilibrium on fabric Activated Carbon (AC) [1]. In order to accelerate the adsorption speed, the effect of ultrasound irradiation on the adsorption kinetics of carbamazepine (CBZ) or ibuprofen (IBP) was studied on ACs of different textures.

Experimental

Three adsorbents were studied: a powdered AC (particles<71 μm), an extruded one formed of cylindrical pellets (3 mm×0.9 mm) made of agglomerated particles (Ø: 1-25 μm), and an AC fabric formed of woven braids (Ø: 750 μm) of yarns (Ø: 295 μm), made of bundles of microporous fibers (Ø: 12.6 μm).
The ACs have been characterized by N_2 adsorption-desorption at 77 K, CO_2 adsorption at 273 K, by density measurements and scanning electron microscopy. The microporous fabric and grains present also an important macroporosity while the powder is both microporous and mesoporous with a negligible macroporosity.
The removal kinetics of CBZ (or IBP) were studied for 400 min (600 min) at C_0=20 ppm (C_0=4 ppm for IBP) at 25 °C in phosphate buffer (pH = 7.4) by adsorption under orbital stirring (20 mg/12 mg of adsorbent in 1 L/0.25 L, stirred at 250 rpm) or by adsorption coupled to ultrasound in a tub at about 40 kHz and 12 W acoustic power. The adsorption kinetics have been simulated by volume diffusion models in order to determine the external mass transfer and volume diffusion coefficients and to compare them with the molecular diffusion coefficients calculated in the studied porous medium.

Results and discussion

The fabric or the granulated AC are weakly damaged after 400 min of ultrasound treatment (<14 % mass. of powder obtained from the grain). The coupling of ultrasound and adsorption for IBP removal shows only an adsorption phenomenon, while for CBZ, both adsorption and degradation by OH° radicals generated by the water sonolysis are observed. The adsorption speed on the AC powder is similar under ultrasound and under orbital stirring.
The sonication of the fabric (or granulated) AC in the tub strongly accelerates the adsorption kinetics of CBZ (C/C_0=0.78 at t=6h) or IBP (C/C_0=0.2 at t=10h) with respect to those obtained under orbital agitation (C/C_0=0.9 at t=6 h for CBZ or C/C_0=0.95 at t=10h for IBP).

Conclusions

The tub sonication enhances the micropollutant transfer speeds within the macroporous network. This can be modeled by apparent diffusion coefficients determined by simulations.

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S10-4

Removal of emerging pollutants present in water using an *E-coli* biofilm supported onto activated carbons prepared from argan wastes

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Introduction:
Recently, the pharmaceutical compounds are been classified as emergent pollutants. According to the literature, paracetamol (PCT) and amoxicillin (AMX) molecules are frequently detected in water bodies [1]. In order to improve the removal rates of paracetamol (PCT) and amoxicillin (AMX) present in water, activated carbons prepared from argan waste were designed as supports for a biofilm based on *E. coli*.

Experimental:
The activation process of carbon materials was carried out using KOH, and H_3PO_4, yielding microporous carbons with high surface areas (2079 $m^2\ g^{-1}$) in all cases. For the preparation of the biofilms supported on the carbon materials, the methodology described by Rivera-Utrilla et al. [2] was used.

Results and discussion:
Adsorption studies without the presence of the biofilm showed rapid kinetics with adsorption constants $k_{PCT} = 0.06$ and $k_{AMX} = 0.007\ min^{-1}$. The adsorption isotherms could be described by the Langmuir isotherm model reaching a maximum adsorption capacity of $q_{PCT} = 502$ and $q_{AMX} = 319\ mg\ g^{-1}$. In contrast, the results obtained for the materials that support the biofilm showed slow kinetics ($k_{PCT} = 0.007$ and $k_{AMX} = 0.003\ min^{-1}$) and a remarkable change in the shape of the adsorption isotherms. In this last case, the experimental data are better represented by a combined Langmuir-Freundlich model, in which three important stages are observed. In a first stage (i), adsorption is carried out in those spaces available after supporting the biofilm in the surface of the ACs; once these spaces have been saturated, a second stage (ii) is present with an exponential behaviour typical of the Freundlich isotherm, which is attributed to the adsorption of the pharmaceutical compounds in the biofilm. Finally, a third stage (iii) is observed where the asymptotic behaviour typical of the saturation of the adsorbent according to the Langmuir model is already appreciated ($q_{PCT} = 504$ and $q_{AMX} = 465\ mg\ g^{-1}$).

Conclusions:
From argan residues, it is possible to prepare activated carbons with specific textural properties as support materials for *E-coli* biofilm. The designed biomaterials show exceptional behaviour in batch-processes for recalcitrant contaminants removal present in water.

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S10-5

Simultaneous adsorption of bisphenol-a and phenol on lignin-derived activated carbons

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Introduction

The presence of organic pollutants in water resources is taking relevance owing to its negative effects on human health, being the adsorption with activated carbons (ACs) one of the most studied technologies to remove these pollutants. Currently, the importance of evaluating synergistic effects among pollutants with the adsorbent in simultaneous adsorption processes is increasing, ensuring their viability at industrial scale.

Experimental

Six ACs were prepared by chemical activation of Alcell® lignin with H_3PO_4 in order to be evaluated as adsorbents for the individual and simultaneous removal of bisphenol-A (BPA) and phenol from aqueous solutions. N_2 adsorption/desorption isotherms at -196 ºC and CO_2 adsorption isotherms at 0 ºC were used to characterize the porous texture. Chemical surface composition was studied by X-ray photoelectron spectroscopy (XPS) and oxygen surface groups were evaluated by CO-CO_2 temperature-programmed desorption (TPD). Equilibrium and kinetic adsorption experiments were carried out at 20 °C.

The effect of the weight impregnation ratio, which varies from 0.3 to 5.0 (H_3PO_4/lignin), and the activation temperature (400, 700 and 900 °C) on the porous texture, surface chemistry and BPA and phenol adsorption on these adsorbents were studied.

Results and discussion

Table 1. Textural parameters and Langmuir adsorption parameters for phenol and BPA adsorption

							Langmuir equation			
Activated Carbon	**A_{BET} (m^2/g)**	**A_t (m^2/g)**	**V_t (cm^3/g)**	**V_{meso} (cm^3/g)**	**$A^{CO_2}{}_{DR}$ (m^2/g)**	**$V^{CO_2}{}_{DR}$ (cm^3/g)**	**q_{phenol} (mg/g)**	**K_L (L/mg)**	**q_{BPA} (mg/g)**	**K_L (L/mg)**
L-0.3-900	623	2	0.284	0.007	825	0.331	52	0.0002	6	0.0004
L-1-900	1151	13	0.501	0.025	840	0.337	165	0.093	13	0.003
L-2-900	1608	20	0.817	0.025	718	0.288	120	0.088	159	0.399
L-5-900	1501	351	0.753	0.575	462	0.185	95	0.040	380	1.044
L-2-400	2550	119	1.175	0.190	856	0.344	97	0.009	615	0.375
L-2-700	1613	14	0.785	0.020	624	0.250	107	0.025	338	1.160

As shown in Table 1, mainly microporous ACs were obtained when lower impregnation ratios (0.3 and 1) were used. At higher impregnation ratios, an increase of the micropore and mesopore volume was observed. ACs with specific surface areas (A_{BET}) from 620 to 2550 m^2/g were obtained. The individual BPA and phenol adsorption isotherms were properly fitted to Langmuir and Freundlich equations. The competitive adsorption of BPA and phenol on ACs was evaluated by simultaneous adsorption of both compounds.

Conclusions

ACs with high porosity development were obtained in this study. The adsorption of BPA and phenol on theses ACs was evaluated, being favored the BPA adsorption.

Acknowledgements

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S10-6

Tuning the surface chemistry of carbon materials to achieve efficient Ni-based catalysts for CO_2 methanation

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Introduction

CO_2 methanation is the reaction in which carbon dioxide (CO_2) reacts with hydrogen (H_2) to form methane (CH_4) [1]. In this work, it is proposed to use carbon materials as supports for Ni nanoparticles, as catalysts for this reaction.

Experimental

Activated carbon (AC) support was modified with nitrogen precursors (urea: AC-UBM or melamine: AC-MBM) and nitric acid (AC-O), to obtain, respectively, N-doped and oxidized ACs and the Ni supported catalysts were prepared by incipient wetness impregnation. The catalysts were fully characterized, and their performance for CO_2 methanation was evaluated.

Results and discussion

¡Error! No se encuentra el origen de la referencia. shows that the sample 15Ni/AC-MBM presents the highest conversion and selectivity to CH_4 among the prepared samples. This might be attributed to the higher N content of this sample. It can also be observed that the oxidation of the support (15Ni/AC-O) leads to an improvement in the performance of the catalysts. The observed trends will be further discussed.

Table 1 – Chemical and textural characterization of the samples and conversion and selectivity values.

Sample	S_{BET} ($m^2\ g^{-1}$)	N content (support) (EA) (%)	$X_{500°C}$ (%)	$S_{CH4,\ 500°C}$ (%)	$S_{CO,\ 500°C}$ (%)
15Ni/AC	653	0	54	33	59
15Ni/AC-U	628	1.24	60	71	25
15Ni/AC-UBM	547	1.83	63	77	22
15Ni/AC-MBM	516	6.20	65	83	17
15Ni/AC-O	634	1.09	62	79	21

S_{BET}-Specific Surface Area; N content (EA)-Nitrogen content (Elemental Analysis); X-conversion of CO_2; S_{CH4}-Selectivity to CH_4; S_{CO}-Selectivity to CO

Conclusions

Tuning the surface properties of activated carbon allowed the improvement of its use as support for catalysts for the CO_2 methanation reaction.

Acknowledgements

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HOT TOPICS

HT1

How next generations of electrochemical capacitors can be developed with help of carbon porosity?

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The most widely known electrochemical capacitors harness the formation of an electrical double-layer (EDL) at the electrode/electrolyte interface as charge storage mechanism. The electrodes are generally made from activated carbons (ACs), owing to their well-developed porosity, high electrical conductivity and low cost. Commercially available EDL capacitors use organic electrolytes, as example tetraethylammonium tetrafluoroborate in acetonitrile, which enable to reach high cell voltage (2.85 V) and consequently relatively high specific energy. However, this technology suffers from serious disadvantages including high cost of the devices manufacturing and environmentally unfriendly nature of the electrolytes. Therefore, alternative concepts of capacitors using "green" solutions are under development.

Recently, we have demonstrated that AC/AC capacitors operating in aqueous medium can perform up to 1.5 V by using an electrolyte with near neutral pH. The extended voltage results from the formation of OH^- ions in the porosity of the negative electrode inducing a high overpotential of di-hydrogen evolution [1]. Later, we have reported about an AC-based hybrid capacitor (HC) developed with a bi-functional aqueous electrolyte which combines a neutral supporting salt (as Li_2SO_4) and a redox-active component (as KI); in this HC, polyiodides are trapped in the porosity of the positive electrode, while OH^- confined in the negative one enable to maintain a cell voltage of 1.5 V. [2]. Owing to hybridization, the capacitance of HC is twice higher than that of a symmetric EDL capacitor made with the same AC. Moving to a concentrated electrolyte made of choline nitrate and iodide, the obtained eco-friendly and low cost HC could operate in a wide temperature range and display a specific energy comparable to EDLCs in organic medium [3].

It is also considered that ILs are attractive for their high electrochemical stability window and negligible vapor pressure. However, their relatively high melting point is an important obstacle for their implementation in EDLCs. In this context, we have studied the effect of confinement in carbon nanopores on ILs melting temperature. By applying 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide – [EMIm][FSI] and a series of carbons with various pore sizes, we have shown that the IL melting temperature is depressed by 32 °C when the IL is encapsulated in a carbon with average pore size ca. 9 nm [4]. Accordingly, EDLCs with electrodes made from such carbon and the $(EMImFSI)_{0.5}(EMImBF_4)_{0.5}$ mixture as electrolyte demonstrated good performance down to -40 °C [5].

Acknowledgements
The Foundation for Polish Science is acknowledged for funding the project TEAM TECH/2016-3/17, and the Polish National Science Centre the MAESTRO project UMO-2016/22/A/ST4/00092.

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HT2

Ageing of carbon based electrochemical capacitors in neutral aqueous electrolyte

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Performance of electrochemical capacitors with activated carbon electrodes is based on the formation of an electrical double-layer. It is strongly affected by the type of electrode material but also kind of electrolytes. A lot of research is devoted to replace organic medium by aqueous electrolyte, especially with neutral pH to limit corrosion effects. A well selected method for cycle life estimation is crucial. The reason of EC failure is elucidated in various electrolytes.

Experimental
Activated carbon materials in the form of powder or tissue (ca. 10 mg per electrode) have been used for EC assembly. Aqueous electrolytes of neutral character such as iodide (1M KI), nitrate (1M $NaNO_3$) and sulphate (1M Li_2SO_4) have been selected. Physico-chemical analyses of carbon materials and electrolytes have been performed prior to the electrochemical measurements. The systems were aged with two methods: galvanostatic cycling and potentiostatic floating. Specific capacitance values have been controlled in time together with internal resistance. After reaching 20% capacitance fade, the systems were disassembled and post mortem analysis such as nitrogen sorption and Raman spectroscopy was performed.

Results and Discussion
Typical galvanostatic charging/discharging with 1 A/g current load and floating tests (with 2h polarization) were performed in various electrolytes. The end-of-life criterion (80% of initial capacitance retained) was the same for two procedures. Both ageing methods performed in 1M KI affect the electrode porosity [1]. Specific surface area of carbon electrodes dropped significantly from 1840 m^2/g to 800 m^2/g, especially for (+) electrode aged by floating (Fig. 1). Floating is much more ageing-effective as its operation time for reaching the same end-of-life criterion is almost 3 times shorter than during cycling. SEM images indicate a deposit on the both aged electrodes independently on the kind of test. This deposit was at the origin of pores blockage, in turn, capacitor failure especially after floating test.

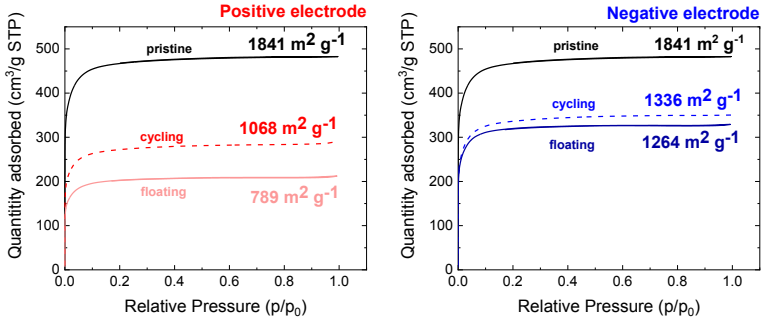

Fig. 1 Post-mortem analysis by N_2 sorption for (+) and (-) electrodes. Electrolyte: 1M KI.

Acknowledgements
This work was supported by the Polish Ministry of Science and Higher Education (Grant No. 03/31/SBAD/0375).

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HT3

Electron conducting cement/carbon nano-composites: expanding concrete structural elements functionalities

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Introduction

Due to a non-negligible ecological footprint that amounts to 5-10% of the worldwide CO_2 emission, cement faces an uncertain future. However, thanks to breakthroughs in science and engineering, cement has a novel potential to contribute to a sustainable development, if besides mechanical strength, new functionalities were added to structural elements in a building. Here we report the synthesis and the characterization of an electron conductive cement/carbon nano-composite able to store electrical energy, and also of interest for heating applications by taking advantage of the Joule effect.

Experimental

First, the preparation of such materials and their electrical conductive properties will be discussed. Then, micro and nano-indentation techniques allowing for the evaluation of the mechanical properties of the nano-composite will be presented. Finally, Cyclic voltammetry experiments to study the potential of the carbon-cement nanocomposites as structural supercapacitors and Joule effect measurements for heating applications will be discussed.

Results and discussion

The reference samples, i.e. pure cement samples and cement samples containing the dispersive agent both behave as electrical insulator. Same goes for cement samples containing less than about 2.5% wt. of carbon nanoparticles. However, for carbon content larger than 2.5% wt., the cement samples show a resistivity significantly lower by about 6 orders of magnitude. The transition between insulator and conductor occurs in a narrow range of concentrations in carbon nanoparticles, which points towards the existence of a percolation threshold above which the carbon nanoparticles form a sample spanning network responsible for the conductive properties. We then leveraged the conductive character of the nanocomposites to assemble a supercapacitor, using our materials as electrodes, leading to a capacitance up to 40 mF/cm^2 for a scan rate of 100 mV/s. Finally, it will be shown that passing a current through the cement/carbon nanocomposites lead to a dramatic increase in temperature which can be controlled by the applied current and the type of carbon used.

Conclusions

We have shown that the addition of carbon nanoparticles allows to turn hardened cement paste into an electrical conductor, without losing the overall mechanical strength of the pure material. Further works have then shown the potential for energy storage of these new conductive materials and their use in heating applications leveraging the Joule effect.

HT4

An asymmetric supercapacitor-diode (CAPode) for unidirectional energy storage

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Introduction

In recent years, benefits of pore size engineering were elaborated: mesopores are of vital importance for the fast transport of ions while micropores contribute to high capacity i.e. charge storage. Desolvation leads to pronounced increase in capacitance if the pore size is smaller than the size of solvated ions. Rationally adjusting the size relationship of electrolyte ions and electrode pores unleashes the full performance of supercapacitors and desalination systems.

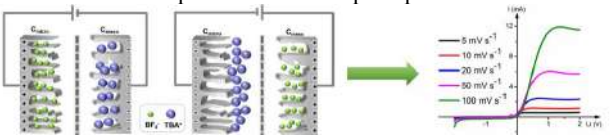

Figure 1. Schematic illustration of the working mechanism of CAPode.

Experimental

Electrochemical performance was investigated by cyclic voltammetry (CV), galvanostatic cycling with potential limitation (GCPL), and electrochemical impedance spectroscopy. The ion-selective adsorption was studied using magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) and *In-Situ* NMR spectroscopy.

Results and discussion

Size-selective microporous carbons (w<0.9 nm) with narrow pore size distribution are demonstrated to exclusively electrosorb small anions (BF_4^-) but size-exclude larger cations (TBA^+ or TPA^+), while the counter electrode, an ordered mesoporous carbon (w>2 nm), gives access to both ions. This architecture exclusively charges in one direction with high rectification ratios (RR=12), representing a novel capacitive analogue of semiconductor-based diodes ("CAPode"). By precise pore size control of microporous carbons (0.6 nm, 0.8 nm and 1.0 nm) combined with an ordered mesoporous counter electrode (4.8 nm) electrolyte cation sieving and unidirectional charging is demonstrated by analyzing the device charge-discharge response and monitoring individual electrodes of the device via *In Situ* NMR spectroscopy (Fig. 1).

Conclusions

By coupling a carbon molecular sieve electrode with an ordered mesoporous carbon a new asymmetric capacitor concept with rectification function and high capacitance is realized. *In situ* NMR spectroscopy proves the size exclusion and unidirectional charging mechanism.

Acknowledgements

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HT5

Perspectives for carbons in environmental applications

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Energy supply and the preservation of the environment are some of the current concerns for society and for the scientific community. Research and development on carbons is aware of that as shown in this congress with the section "Carbons for Environmental Applications". Starting from the fact that carbon is a unique element which can form several and very different nanostructures, the research in carbon materials is tremendously broad and covers numerous applications, most of them related with the environmental. Among them it can be highlighted the following topics that will be covered in this session of hot-topics: adsorption, catalysis and bio-carbons.

Taking advantage of the possibility of porous properties of carbons, maybe one of the oldest uses of carbon materials is as **adsorbent of pollutants either in gas or liquid phase**. Maybe one of the most interesting researches in this area nowadays is their use for separation of mixture of gases such as CO_2/CH_4 (from biogas production processes) or CO_2/N_2 (in post-combustion systems) for further storage of CO_2 and valorisation of the CO_2, CH_4 and the rest of gases of the stream. Regarding to the use of carbons in liquid phase, the most relevant issue is related to water and wastewater treatments, where carbons are use as adsorbent or catalyst to eliminate different pollutants, being the inhibition of nitrification of water a current serious concern due to the massive use of fertilizers in agriculture. One of the hot-topics selected for this section of "Carbons for Environmental Applications" deals with this problem. However, it can be said that carbon materials are mainly used, in their several forms, as catalyst or support for **catalytic reactions**. This application covers many different catalysis from stablished industrial processes to new emerging technologies. Always searching more efficient, cleaner and cheaper processes, even avoiding traditional catalyst based in the expensive noble metals. The electrolysis of water for H_2 generation, besides the use of carbons in electrochemical applications (i.e. energy generation and storage) has a great interest nowadays and they are covered in other section of CESEP'19. Especially interesting is the photocatalysis that combines a catalytic process with renewable energy, the production of biofuels, and methanation reactions, which besides the elimination of CO_2, the production of fuels such as CH_4 or H_2 are pursued. The other hot-topic of the section "Carbons for Environmental Applications" addresses this topic, combining methanation reaction with new strategies for carbon monoliths production by 3D printing. The use of **bioresources for carbon materials** production has also relevance, since it is a way of either using renewable and/or cheaper resources or they are a way for waste valorisation and could be included in a biorrefinery scheme where liquids (chemicals), gases (energy and chemicals) and solids (carbon materials) would be obtained by different thermochemical processes. In fact, catalysts produced from biomass could be use in the catalytic conversion of chemicals from biomass in a biorrefinery context. Special mention has to be paid to the use of carbons for **biotechnological applications**, as supports for enzymes, drug delivery, magnetic carbons, scaffolds for growing tissues, etc.

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HT6

Carbon monoliths with designed morphology and tailored textural properties for environmental catalytic applications

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Introduction

Monoliths with cellular geometry are widely used in the industry. However, the geometry of these monoliths is limited to designs obtained by extrusion, usually composed of straight and parallel channels [1]. In the present work, the use of 3D printing technique combined with carbon preparation procedures is proposed as an alternative route to obtain carbon monoliths with designed morphology and tailored textural properties for catalytic applications.

Experimental

Carbon monoliths (CM) were prepared by polymerization and subsequent carbonization of resorcinol-formaldehyde (RF) hydrogels with different water (W) compositions (R:W molar ratio=1:15 and 1:17) [2]. Two types of templates were designed by 3D printing: D1, with straight channels and, D2 with tortuous channels. The CM were impregnated with the CuO/CeO_2 active phase, characterized, and tested as catalysts in CO-PrOx reaction.

Results and discussion

Figure 1 presents an image of the CM design D2. The tortuosity followed by the gases through this CM_D2 monolith could induce the gases to a turbulent regime, improving the access to the active phase and its catalytic activity, as it can be observed in Figure 2a, where the different designs of the carbon monoliths are compared with a cordierite monolith. In addition, in Figure 2b, it is observed that the monolith with the best catalytic performance is the monolith prepared with lower R:W ratio, pointing out the importance, also, of the monolith's textural properties.

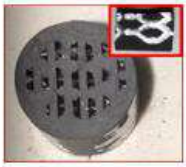

Figure 1. Carbon monolith (CM_D2)

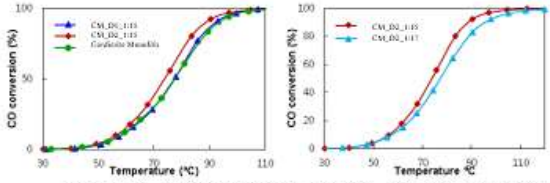

Figure 2. CO conversion profiles for CM with (a) different monolith designs and; (b) different R:W ratios

Conclusions

High performance carbon monoliths with designed morphology and tailored textural properties were synthetized by combining 3D printing technique with carbon preparation procedures. This procedure developed in the present work, opens the gate to the synthesis of designed catalysts due to the versatility presented by carbon materials and 3D printing techniques.

Acknowledgements

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HT7

Adsorption kinetics of nitrate ions on activated carbons

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Introduction

The development of activated carbons (AC) produced from biomass residues for the removal of pollutants, specifically nitrate ions in water, is recognized as the cheapest and most effective material and furthermore it is easy maintenance [1]. However, in the nitrate removal processes for industrial applications, the specific characteristics of adsorbents have to be improved. Recent studies showed that the adsorption capacity of activated carbons for nitrate ions can be promoted by playing on the surface chemistry and textural characteristics of activated carbons [2].

In this study, to better understand the mechanisms of nitrate ion adsorption, the adsorption kinetic and adsorption capacity of nitrate ions were performed on commercial activated carbons having either acidic or basic functional groups and different types of pores. In order to model the nitrate ion adsorption, Ho and Mc Kay kinetic model and Langmuir model were used.

Experimental

Commercial activated carbons provided by Jacobi Carbon® were studied. Three of them (L27, X17 and S21) were selected taking into account their porosity and surface chemistry. To optimize the adsorption kinetic and adsorption capacity of nitrate ions, the influence of various parameters, such as pH and temperature of the nitrate solution, the nitrate initial concentration and also the effect of competing anions, such as phosphates, carbonates, sulfates and chlorides was studied. Nitrate concentrations were determined by chemiluminescence (TOC-L CPH, Shimadza).

Results and Discussion

Concerning the porous texture of AC, L27 material presents the broadest distribution with high mesoporous and microporous volumes. X17 material has a microporous volume poorly developed and S21 material is essentially microporous. As for the surface chemistry characteristics of the AC, L27 material has acidic surface groups, whereas X17 material has basic functional groups and S21 material has low amounts of acidic and basic oxygenated groups, hence has a neutral character.

The adsorption kinetics show the importance of initial pH on the nitrate ions removal. Only at basic pH, the nitrates can be adsorbed on L27 and X17 materials. The low adsorption of nitrates at acidic pH=2 is related to the competition of Cl^- ions with nitrate ions (Cl^- coming from HCl, added to adjust the pH). The surface charge being positive ($pH < pH_{PZC}$) and Cl^- ions being smaller, they are adsorbed at first. The highest nitrate adsorption occurs at pH =9, even with a material having a negative surface charge ($pH > pH_{PZC}$). In this case, a surface protonation and the repulsion of the Cl^- ions allow a better NO_3^- adsorption. Ho and Mc Kay kinetic model and Langmuir model used to model the nitrate ion adsorption will be discussed.

Acknowledgments

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POSTER COMMUNICATIONS

P1

Screening of nanoporous carbons for the storage and separation of strategic gas mixtures

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Introduction

There is an urgent demand to develop efficient strategies for the separation/storage of gases of strategic impact with minimal environmental impact and affordable costs. Among different adsorbents, nanoporous carbons display lower adsorption capacity and selectivity than other adsorbents, but they are still considered a viable option due to their relatively low cost and easy regeneration (compared to MOFs and zeolites). The objective of this work was to carry out a screening of nanoporous carbons of different nature for gas storage and separation (natural gas purification, biogas upgrading and CO_2 separation from flue gases) compared under realistic experimental conditions. To attain this goal, we have prepared nanoporous carbons with well-defined nanopore architectures from various precursors, and assessed their capacity for the storage and/or separation of gases of strategic impact, including CO_2, CH_4, and their mixtures.

Experimental

N-doped nanoporous resins were synthesized by the sol-gel polycondensation of various deep eutectic solvents prepared by physical mixture of resorcinol, choline chloride and a nitrogen source (e.g., urea, thiourea, 1-(3-hydroxyphenyl) urea, 1,1-Dimethylbiguanide hydrochloride), as indicated elsewhere [1,2]. The adsorption capacity of the carbons prepared towards CO_2 and CH_4 at room temperature was evaluated from equilibrium adsorption isotherms in dry and humid conditions. The selectivity in gas mixtures of different composition was evaluated using IAST predictions.

Results, Discussion and Conclusions

The DES-assisted polycondensation of the reactants allowed to produced nitrogen-doped carbons while different N-moieties and nanopore architectures. The non-carbonized materials showed a low porosity and moderate uptakes of carbon dioxide, but poor performance under humid conditions due to the high functionalization. The carbonized materials showed large gas uptakes due to the increase in narrow microporosity, and an almost negligible impact of moisture in the gas uptake of the studied gases over several cycles. The selectivity towards carbon dioxide over methane of the carbons is still quite high, despite the decrease in the nitrogen content upon pyrolysis.

Acknowledgements

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P2

CO_2 capture by mesoporous carbons produced from low value coal tar-derived products

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Introduction

Carbon capture and storage (CCS) is considered one of the main technologies to reduce CO_2 emissions, according to the IPCC report [1]. The adsorption-desorption CO_2 separation process with activated carbons (ACs) is very promising due to the high surface area, low regeneration costs and good CO_2 capture capacities of the ACs materials [2]. In this work, ordered mesoporous ACs obtained from coal-tar rejects, allowing the revalorization of distillation coal liquid rejects, are evaluated for CO_2 capture.

Experimental

Mesoporous carbon materials were obtained using the hard-templating method, with SBA-15 as ordered template and creosotes as the carbon precursor in acidic medium, following the methodology described elsewhere [3]. The carbon materials were chemically and physically activated, by using different KOH/C ratios at different temperatures and CO_2 before and after eliminating the template, respectively. The CO_2 capture capacities of obtained carbon materials were measured at 25 ºC and 90% of CO_2. Different adsorption temperatures (25-150 ºC) and different CO_2 concentrations (5-90 %) were evaluated for the best samples.

Results and discussion

Figure 1 shows the CO_2 capture capacities at 25 ºC of the mesoporous carbons. The chemically activated sample at 850 ºC and with a KOH/C ratio of 1:4 showed the best CO_2 capture capacity, 2.48 mmol CO_2/g AC. The best physical AC was the one obtained under the highest activation time and with the elimination of the template after the activation process, 2.38 mmol CO_2/g AC. Both samples present the highest surface areas and the highest micropore volume percentage. However, the micropore volume (0.62 cm^3/g) is lower than other ACs with similar CO_2 capture capacities.

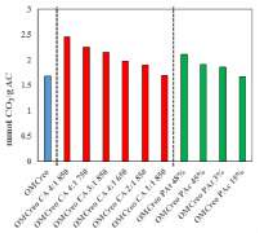

Figure 2.- CO2 capture capacities at 25 C of the different ACs

Conclusions

Mesoporous ACs have been evaluated at 25 ºC. Among them, the best chemically and physically ACs show CO_2 capture capacities that can be comparable with commercial ACs and previous reported ACs (2.5 mmol CO_2 / g AC), all of them with a higher micropore volume.

Acknowledgements

This project has received funding from the Research Fund for Coal and Steel (RFCS) of the European Union (EU) under grant agreement No 709741.

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P3

Confinement Effects in the Formation of Ice/Gas Hydrate Nanocrystals evaluated using differential scanning calorimetry (DSC)

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Introduction

The freezing and melting processes of water in confined media have attracted the interest of the scientific community along the years. The interaction between the water and the pore walls of the material modifies the free energy of the liquid inside the pore. Generally, a depression in the water melting temperature is observed, this decrease being proportional to the inverse of the pore radius [1]. Such phenomenon has been already reported in adsorbent materials, mainly mesoporous silica particles, since they present a very uniform arrangement with a well-defined porosity.

However, confined water could also experience different and important changes when is subjected to external stimulus, for example CH_4 pressure. In this context, the combination of water with high pressure of CH_4 at low temperatures would lead to the nucleation and growth of CH_4 hydrates nanocrystals. These structures, which are also found in nature, are certainly considered as potential CH_4 storage systems since 1 m^3 of hydrate can release up to 180m^3 of CH_4 [2]. Recently, our research group already reported that by impregnation of the carbon with water, the final CH_4 capacity significantly increased compared to the capacity of the dry carbon due to the CH_4 hydrates formation at 2 ºC [3,4].

Thermodynamically, at low temperatures, both structures (ice and hydrate) could coexist. From our knowledge, there is little information when both phases are present in the porosity of an activated carbon and how the confinement effects modify the co-existence of these phases.

Experimental

The activated carbon was impregnated at different water contents and evaluated by DSC in order to determine the melting and freezing points of confined water. Additionally, the water saturated carbon was also analyzed under external stimulus such as high N_2 and CH_4 pressure. Also, N_2, CO_2 and H_2O vapor isotherms at -196ºC, 0ºC and 25ºC respectively, were performed.

Results and discussion

The DSC scans suggest that adsorbed water in narrow micropores does not undergo any ice crystallization while water in mesopores freezes at -40ºC degrees, quite below bulk water. When confined water is pressurized with CH_4, hydrate formation is observed without any ice formation up to saturation (water to hydrate conversion is almost 100%). Although thermodynamically both phases must coexist, confinement effects promote the conversion to pure hydrate.

Acknowledgements

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P4

Adsorption of organic compounds on lignocellulosic-derived spherical activated carbons

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Introduction

The performance of activated carbons (AC) in a wide range of applications depends both on their physico-chemical properties (porosity, surface chemistry, mechanical strength), and on their morphology (powdered, granules, spheres, …). The objective of this study is to prepare spherical materials from lignocellulosic residues of different origin/composition, which implies simultaneous wastes' minimization and valorization, and to use them in formaldehyde adsorption from gaseous streams. These materials are compared with other ACs with different morphologies, porosities and surface chemistry to analyse the effect of these parameters.

Experimental

Several spherical seeds (from *Phoenix Dactylifera (PD), Rhamnus Alaternus (RA)*, *Osyris Lanceolate (OL)* and *Canna Indica (CI)*) were selected to obtain spherical ACs. In each case, the raw material was dried (110°C, 12 h) and carbonized in a tubular furnace (100 ml/ min N_2, 5°C/min heating rate up to 850°C, 2 h) [1]. The obtained char was activated in a tubular furnace with CO_2 (80 ml/min) at 850°C (5°C/min heating rate) held for 10 h [1]. The obtained materials are named, respectively, *PD*-A, *RA*-A, *OL*-A and *CI*-A. Porosity, morphology and mechanical strength were characterized, as described in [1]. For comparison, other commercial activated carbons were selected: Mead Westvaco WVA1100 (granular, 10x25 mesh, 1796 m^2/g) and Kureha (spherical, 0.75 μm, 1185 m^2/g). For the fixed bed adsorption tests, 30 ml/min formaldehyde (450 ppmv in N_2) flow and 0.1 g AC were used. The tests were carried out at room temperature after 12 h purging in air.

Results and discussion

Carbonization and activation of three of the studied precursors, *PD, RA* and *CI*, leads to spherical ACs, showing good mechanical properties and a remarkable porosity development (S_{BET} ranging 400-900 m^2/g). The highest activation yield, 17 %, is obtained for *PD*-A. Formaldehyde adsorption showed that, in the conditions studied, large porosity developments and, especially, low surface chemistry contents are desired. The formaldehyde adsorption capacity of *PD*-A is remarkable, and similar to that of WVA1100 (3.28 and 3.03 mg formaldehyde/g AC for *PD*-A and WVA1100, respectively, after 6 h test), despite its much lower porosity, what can be explained as a result of its lower surface oxygen content.

Conclusions

After carbonization and activation, three of the selected precursors maintain the spherical morphology of the lignocellulosic precursor. Formaldehyde adsorption is favored in ACs with low surface oxygen content. The activation yield of the *PD*-A spherical AC is over two times larger than that of *RA*-A and *CI*-A and its capacity for formaldehyde adsorption is similar to that of the WVA1100 commercial AC.

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P5

High-surface area zeolite templated carbon (ZTC) materials for methane storage

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Introduction

In recent decades, there has been an increasing interest to develop gas storage systems for energy purposes. In this sense, high pressure adsorption (physisorption) on highly porous sorbents appears to be an interesting approach to store gases [1]. In general, for this application, adsorbent requires a high porosity development, large micropore volume, small average pore size and high packing density. In this study, the carbon monoliths were prepared from ZTC and KOH-activated carbon (MSC30) via hot pressing using a small amount of binder in order to increase their density and mechanical properties. As a result, ZTC monolith is more densified, thus achieving higher methane storage.

Experimental

The carbon monoliths were made from ZTC and MSC30 using different binders such as carboxymethylcellulose sodium salt (C), methylcellulose (M) and bentonite (B). With the aim of finding out the optimum conditions for the monolith preparation, the effects of type of binder (C, M and B), the compaction pressure (132 and 350 MPa) and temperature (160, 300 and 400 °C) were analyzed. For monolith preparation, the corresponding amounts of pulverized carbon material and an aqueous solution of binder were first thoroughly mixed, and then the water content present in the slurry was removed by heating. Finally, the resultant mixtures were compressed at 132 or 350 MPa under vacuum at 160 °C, 300 or 400 °C, respectively, followed by cooling to RT. The prepared samples were analyzed by different technique (gas adsorption, SEM,…). CH_4 adsorption was measured at RT up to 40 bar with a fully automated volumetric apparatus (iSorbHP2).

Results and discussion

Table 1 contains the texture characterization results together with the piece densities of the pristine and the carbon monoliths obtained from them. From these results, it can be seen that the bulk density of ZTC monoliths was rapidly increased from 0.17 to 1.13 g/cm^3 by increasing the pressure and the temperature of hot pressing. On the other hand, the density of MSC30 monolith is found to be in the range of 0.60 g/cm^3. For the MSC30, the change in the porosities before and after hot pressing was small.

However, the porosities of ZTC were greatly decreased. The CH_4 storage of the carbon monoliths on a gravimetric basis depends on the textural properties, but the volumetric basis storage depends on both the textural properties and densities.

Samples	S_{BET} (m^2/g)	V_{N2} (cm^3/g)	V_{CO2} (cm^3/g)	Density (g/cm^3)	CH_4 uptake*	
					(wt%)	(g/L)
MSC30	2690	1.18	0.54	0.24	20	48
ZTC	3730	1.75	0.56	0.17	22	37
MSC30-C-160-132	1960	1.03	0.54	0.47	22	102
ZTC-M-160-132	2527	1.06	0.58	0.60	19	113
ZTC-B-300-350	1328	0.54	0.47	0.90	9	77
ZTC-B-400-350	807	0.33	0.28	1.13	6	71

Conclusions

ZTC monolith is more densified, thus achieving higher volumetric methane storage.

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P6

Surface functionalization of activated carbon fibre from Opuntia Ficus-Indica for enhanced adsorption of herbicide from aqueous solutions

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Introduction

The search for adsorbent materials with a large surface area, porosity, good adsorbent–adsorbate affinity, good sensitivity and low cost has been increasing more and more towards the adsorption of non-specific analytes.

Experimental

The natural (ACF) was cut into slices, which dried at 150 °C for 12 h, the ACF samples were grinded in a mortar with a pestle, then the received sample (ACF-T) was washed in distilled water, filtered, and dried for further evaluation. After, were then fully impregnated for 4 hours by HCl 1M. Here, HCl acted as pore-forming agents thereby improving the specific surface area of the material (ACF-TA).

Results and discussion

The nitrogen adsorption/desorption isotherms at 77K for ACF-T and ACF-TA samples and detailed data are listed in this Table.

Samples	S_{BET} / $m^2.g^{-1}$	V_{DR} (N_2) / $cm^3.g^{-1}$	V_{meso} / $cm^3.g^{-1}$
ACF-T	102.82	0.12	0.04
ACF-TA	184.69	1.87	0.13

Conclusions

The adsorption behavior of (Vng) on ACF-TA and on ACF-T was studied as a function of the concentration of the adsorbate, contact time and nature of adsorbent. Analysis of the results shows that the (Vng) adsorption process on ACF-TA was increased as the initial concentration of (Vng) increased. Furthermore, the effect of contact time was conducted and the balance time was achieved at 2 hours.

Acknowledgements

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P7

Biochars as matrix for slow release urea

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Introduction

When applied to soil urea can suffer nitrogen losses which are harmful to the environment and reduce fertilization efficiency [1, 2]. The aim of this work was to synthesize materials to allow slow release urea (SRU) by dispersing urea in carbon matrices from different waste biomasses thus maximizing urea fertilization effectiveness.

Experimental

Carbon matrices prepared in different conditions (400, 600, 800 °C/0.5; 1; 2 h) from coconut husk, sugarcane straw and bagasse were impregnated with urea by melting (133 °C/1h) producing 27 SRU in total. Slow release performance was assayed by static bath tests adapted from HG/T 23348-2009 method (China).

Results and discussion

All SRU materials had slower release than conventional urea (Figure 1), with an outstanding performance of the matrix from sugarcane straw (400 °C – 0.5 h) that had the lowest initial release (≈ 17 % wt./wt.) (Figure 1 A) and released less than 50 % at end of the test.

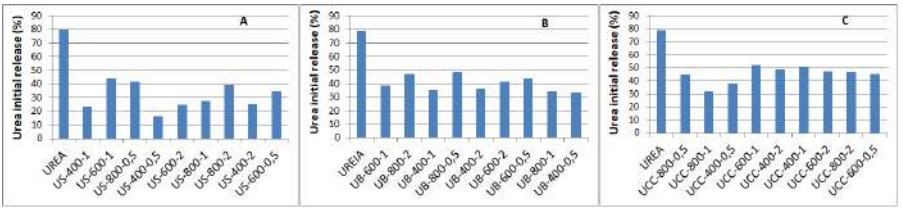

Figure 1 – Release behavior of the synthetized SRU materials (code: Ubiomass – Temperature – Time). A – SRU from sugarcane straw biochars; B - SRU from bagasse; C – SRU from coconut husk.

Conclusions

All SRU materials delayed urea release, specially, the SRU from sugarcane straw (400 °C – 0.5 h), which seemed to be a promising material that should be explored in plant growth tests.

Acknowledgements

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P8

Surface functionalization of (o-phenylenediamine)-co-Aniline and these properties

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Introduction

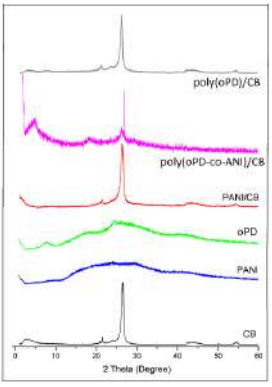
Composites obtained by deposition of conducting polymers (CPs) over Carbon Black (CB) particles, showed thermal stability and effective reduction of the surface area and pore volume of the CB [1, 2].

Experimental

The composites were prepared by maintaining CB under mechanical stirring for 2 hour in contact with acidic aqueous solutions of 1.0M monomer in 1.0M HCl. After that, the solution of 0.25M APS in 1.0M HCl was drop wise added to the monomer solution and the reaction occurred for 24 hours. After the chemical polymerization, the resulting powder was washed with 1.0 M HCl solution and dried at 60 °C for 24 hours.

Results and discussion

This figure shows the X-ray diffraction patterns of the CB, PANI, poly(oPD), PANI/CB, poly(oPD-co-ANI)/CB and poly(oPD)/CB nanocomposites



Conclusions

A simple method to prepare CPs/CB composites by the direct chemical polymerization of ANI and/or oPD in the presence of a CB dispersion under stirring was described.

Acknowledgements

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P9

Optimization of carbon structure in xerogels for different electrochemical applications

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Introduction

Carbon xerogels are porous materials which properties may be designed in order to fit the requirements for their final application. Thus, they are candidates to be used as active materials in electrochemical devices as supercapacitors, batteries or fuel cells, although the required characteristics differ considerably from one device to another.

Experimental

Carbon xerogels were obtained by polymerization of resorcinol and formaldehyde in a sol-gel process assisted by microwave heating. During the sol preparation, graphene oxide could be added as a stable suspension. The polymers obtained were dried and submitted to different thermal treatments: (i) activation at 1000ºC with CO_2, or (ii) heated in inert atmosphere up to 2800ºC for graphitization process. Samples were texturally characterized and their behavior tested in different electrochemical devices: supercapacitors, Li-ion batteries and in the oxygen reduction reactions involved in fuel cells.

Results and discussion

Carbon xerogels were obtained by a fast and cost-effective method, with no impurities, and desired pore size for the different devices. A sample with narrow mesopores and ca. 1500 m^2/g containing graphene imbibed in the structure exhibited greater electrical conductivity, energy and power density than the commercial YP-50F as active material in supercapacitors with aqueous electrolyte. On the other hand, a carbon xerogel containing graphene, with wide macropores and relatively high ordering degree, displayed higher capacitance and stability than the commercial SLP50. Finally, activated carbon xerogel with a good combination of microporosity and feeder pores seemed to be a good support for nitrogen and iron, and thus a substitute to the expensive platinum as electrocatalyst in fuel cells.

Conclusions

The incorporation of graphene oxide into the structure of the xerogel confers to the sample a high electrical conductivity and a great influence on further ordering of the carbon structure. Thus, samples perform very well as active material in supercapacitors and Li-ion batteries in comparison to commercial references. In the case of fuel cells, activated carbon xerogels may also be good supports for active phases, being relevant the surface chemistry.

Acknowledgements

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P10

Influence of polymerization conditions on carbon xerogels porous structure

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Introduction

Carbon gels are porous materials that can be obtained through a cost-effective process based in microwave heating [1]. Their porous characteristics may be finely tuned for a certain application by modification of the chemical variables [2]. However, the porosity in carbons is usually characterized just by the pore size and volume of pores, and other characteristics such as pore tortuosity would be a relevant property that will have also a great influence on certain applications, especially when viscous fluids are involved and pressure drops or residence times of fluids passing through the bed should be controlled.

Experimental

A series of resorcinol-formaldehyde (RF) gels were obtained by a sol-gel process performed under microwave heating. Different combinations of R/F ratio, dilution, methanol content, pH of the precursor solution were used for obtaining polymers with different porous structure but maintaining analogous chemistry composition. The polymers were carbonized and textural characterization was performed by N_2 adsorption-desorption isotherms, Hg porosimetry and SEM.

Results and discussion

Carbon xerogels with similar mean pore size can be obtained by a compensating effect of decreasing pH while decreasing the dilution, or decreasing the pH while increasing the methanol content of the precursor solution. Therefore a series of pairs of samples were obtained by different combination of variables and with a mean pore size of 30, 100 and 300 nm. However, these pairs showed noticeable differences in their porous structure. Parameters such as tortuosity and permeability obtained from Hg porosimetry show very different values. SEM characterization of the samples reveals that certain combinations of the variables brings about polymeric clusters in RF gels that seem to be merged leading to straight channels with evident less pore tortuosity and therefore higher permeability of the materials.

Conclusions

Controlling the synthesis conditions of RF gels allows not only designing the mean pore size of the final carbons but also the pore structure connectivity (i.e. tortuosity modulation). This property plays a key role in many applications such as separation processes.

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P11

Synthesis and characterization of activated carbons from Algerian coal

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Introduction

Activated carbon (AC) is perhaps one of the most widely used adsorbents in recent years.For decades,. It is now considered one of the best adsorbents available to remove trace organic and inorganic contaminants. Its can be divided into several categories: effluent treatment, drinking water treatment, solvent recovery, air treatment, discoloration... This explains the growing market trend towards the use of activated carbons[1].

Experimental

Two coals Menouna (M) and Didi (D) from the Saoura region (South-West Algeria, wilaya of Béchar).M and D were impregnated with potassium hydroxide (3.92 10^{-2}mol/g), for 24 hours and pyrolyzed at 800 ° C under flowing nitrogen, they are named MK and DK. Carbons have been characterized by textural (N_2, CO_2) morphological (SEM, TEM) and chemical (FTIR and XPS) characterization.

Results and discussion

Pyrolysis in the presence of potassium hydroxide develops very high BET specific surfaces:2264 and 1982 $m^2.g^{-1}$ for MK and DK, respectively. At high temperature, the resulting carbonate reacts with coal by giving carbon monoxide and metallic potassium[2].

Using SEM, the MK and DK coals have cavities with openings of about 2µm.TEM analysis shows that they have a nanometric structure.

Conclusions

The addition of KOH significantly enhances the porous texture, particularly in the case of MK coal, where SBET exceeds 2250 m^2/g; a good dispersion, at low temperature, of this additive in the coal followed by activation at higher temperature enhances the porous texture.

In conclusion, the results show that MK and DK coals are characterized by very interesting adsorption properties, they can be excellent adsorbents for compounds of molecular diameter covering a wide range.

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P12

Preparation and characterization of activated carbons from Baobab and Balanites shell stones and their use for diazinon removal

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Introduction

Large amount of chemicals are often used for the preparation of Activated Carbons (ACs) by the activation of biomass [1]. This study evaluates the performance of ACs produced by using small amount of KOH for the removal of diazinon: an organophosphate insecticide frequently polluting the groundwater wells in West Africa.

Experimental

ACs were prepared from impregnated granular precursors (Adansonia digitata, i.e. Baobab shell seeds and Balanites aegyptiaca shell stones) with a biomass/KOH ratio of 0.2, pyrolised in the range 800-870 °C under nitrogen flow for 2h and further extensively washed in water and dried. Their characterization has included elemental analysis, infrared spectroscopy, TGA, XPS, SEM, N_2 adsorption-desorption at 77 K and CO_2 adsorption at 273 K. Kinetics of the removal of diazinon and its hydrolysis product: 2-isopryl-6-methyl-4-pyrimidinol (IMP), were studied on the prepared ACs (20 mg) at 2 ppm and 20 ppm initial concentrations stirred in tap water (1L) in an orbital shaker (250 rpm).

Results and discussion

Thermal analyses have demonstrated that precursors presented similar thermal degradation profiles with slightly different biopolymers contents. Both prepared ACs were microporous (pore size lower than 2 nm) with BET surface areas (S_{BET}) around 1249 m^2/g for Baobab precursor and 1209 m^2/g for Balanites one. No relevant differences or changes have been detected on the surface chemistry of both ACs. pHs of point zero charge are close to neutrality for Baobab (6.93) and Balanites (6.29) ACs.
The diazinon removal is mainly due to the adsorption in the first hour and its hydrolysis is the preponderant phenomenon observed after one hour. Compared to diazinon (Q_{ads}~50 mg/g at C_0=2 ppm), IMP is weakly adsorbed on ACs (Q_{ads}~15 mg/g at C_0=2 ppm) despite its polarity.

Conclusions

Results brought out a relationship between the S_{BET} of the ACs and the kinetics of diazinon removal by adsorption.

Acknowledgements

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P13

Waste marble dust: An interesting residue to produce cement

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Introduction

Besides resolving the problem of its disposal, the main reason to use marble dust in cement mortar and concrete is that it improves the cohesion of fresh concrete [1]. The objective of the present study was to establish the technological and regulatory viability of using marble industry waste as additive in Portland cement, as well as evaluate the material using two environmental categories: global warming potential (GWP) and primary energy demand.

Experimental procedure

The experimental objective of this study was to prepare hydraulic cement by mixing industrial clinker, natural plaster, and marble dust waste obtained from ornamental marble processing. According to the objectives of this study, the percentage addition of marble dust is the same as the percentage reduction in clinker, so that the water: cement ratio is not changed, and plaster alone is added as setting regulator.

Results and discussion

Physicochemical analysis confirmed its feasibility as a pure and clean by-product. The paste workability varies according to the percentage addition, and water percentage values are similar to or lower than those in the control series. Initial and final setting times are altered when the cementing mixture contains 10 % marble dust. Expansion values of samples with marble dust addition are the same as those of the control series, with samples M-2, M-4, and M-6 reaching a value of 1 mm.

Flexural tensile strength test results at 365 days are identical for samples M-1, M-2, and M-3 to those for the control series. Flexural tensile strength data are always lower for samples M-4, M-5, and M-6 than for the control series, although this difference is reduced at higher curing ages.

Compression resistance is higher in samples with marble waste percentage additions up to 10 % than in the control series. Compression resistance at curing ages of 90 and 365 days was> 50 % of reference resistance values at 28 days. No published study reached the age of 365 days and few exceeded 28 days.

Conclusions

The cementing mixture presented meets physicochemical criteria for the utilization of marble dust as by-product in the preparation of CEM-II cement. Moreover, i) It meets the criteria inUNE-EN 196-3 for any resistance class according to tests conducted on the cementing paste in fresh state, ii) It can be classified as CEM-II in accordance with RC-16 guidelines, with aresistance class that varies as a function of the percentage addition of marble dust.

Finally, with respect to the technical feasibility of using ornamental marble fabrication waste as additive to clinker to form a cementing mixture, the optimal percentage addition is 10 % to obtain CEM-II (32.5 N), CEM-II (32.5 R), and CEM-II (42.5 N).

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P14

A novel method for the synthesis of graphene nanostructures by atmospheric-pressure microwave plasma

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Introduction

The most common methods to obtain graphene-based materials at relatively large scale are chemical vapor deposition and Liquid Phase Exfoliation, both of them presenting several limitations [1]. Among other processes, the use of microwave plasma techniques is an interesting technological alternative for the synthesis of carbon-based nanomaterials -including the fabrication of graphene derivatives- [2], due to the possibility to operate at atmospheric-pressure, and the lack of supports or catalyst, for which the amount of residues generated is considerably reduced. Taking this into account, the aim of this work is the optimization of the production of graphene-based materials through the decomposition of ethanol by microwave plasma, exploring the impact of various operating conditions in the reaction yield and the features of the prepared materials.

Experimental

An atmospheric microwave plasma torch is developed using a magnetron at 2.45 GHz (300 W) through argon discharges created by a TIAGO (*Torche à Injection Axiale sur Guide d'Ondes*) torch [3]. Ethanol is used as the carbon source, which decomposition in the plasma renders a solid fraction with graphenic characteristics. The carbon source is incorporated in the reactor coaxially respect of the waveguide, using ca. 1 L/min of argon to sustain the plasma, and variable flows of ethanol (ca. 2.0-4.0 g/h) to obtain volume fractions of ethanol between 2.1-4.1 v/v.%.

Results, Discussion and Conclusions

The optimization of the operating conditions of the plasma has shown that the ratio EtOH/Ar flow (v/v.%) has a strong influence on both the yield of the solid fraction, and the structural characteristics of the obtained graphene-like materials. In this regard, the maximum production of carbon material has found for a flow of carbon source of ca. 3.4 g EtOH/h, being about 30 mg/h more productive than the least effective synthetic conditions evaluated. The characterization of the solid fraction confirmed the importance of the control of the synthesis conditions (particularly the plasma feed) on the structural order of the obtained carbon material, with differences ranging from the production of few layer graphene to a mixture of carbon nanotubes and graphene layers.

Acknowledgements

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P15

Effect of the Isomer in the Electrochemical Incorporation of N and P Functionalities in Carbon Nanotubes

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Introduction

The chemical functionalization of carbon nanotubes (CNTs) with heteroatoms has gained increasing attention for the development and improvement of environmental and energy related applications. The tailoring of the surface chemistry permits to decrease the reactivity of the carbon material or to create specific active sites for different electrocatalytic reactions. In this sense, electrochemical methods allow a greater control in the modification of the CNTs without damaging the structure and properties of the pristine material.

Experimental

Electrochemical modification of SWCNT was carried out by anodic polarization at different potentials in presence of 2 and 4-aminophosphonic acid (APPA) monomers, based on the procedure described by González-Gaitán et. al [1].

Results and discussion

Electrochemical functionalization of SWCNTs has been achieved through the formation of electroactive species by electrooxidation of the 2- and 4-APPA. Depending on the phosphonic acid employed and potential applied, presence of different surface redox processes, increase in the double-layer capacitance and degree of modification with P and N-containing species are observed. Interestingly, an applied potential of 1.4 V is the optimum value to reach the highest amount of P-loading on the CNTs surface.

Conclusions

N and P-containing species were incorporated on SWCNTs by electrochemical methods with good control over the amount of species loaded on the carbon material.

Acknowledgements

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P16

Effect of electrode composition and electrolyte flow in electrochemical regeneration of activated carbon in a kilogram batch reactor

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Introduction

Electrochemical regeneration of activated carbon (AC) is a greener alternative to the thermal regeneration methods due to the reduction of CO_2 emissions and lower energy consumption [1-2]. The main disadvantage is the difficulty for reproducing it at large scale. The aim of this work is to analyze the effect of anode composition and electrolyte flow on the regeneration efficiency of AC by electrochemical methods in a kilogram batch reactor.

Experimental

The electrochemical batch reactor has been built to treat 15kg of spent AC supplied by municipal DWTP. To analyze the effect of the electrode composition, experiments have been carried out using Pt/Ti, Ti/RuO_2 and Ti/IrO_2 as anodes and stainless steel as cathode. The working current was 70A (corresponding to a current density of 0.025 A/cm^2), it was applied for 4h and 0.5M H_2SO_4 was used as electrolyte solution. Experiments were carried out at 300, 500, 750 and 1000 L/h. To verify the regeneration treatment, physicochemical characterization of the AC was determined by physical adsorption of gases, temperature programmed desorption and SEM images. The electrolyte solution was analyzed by UV-VIS.

Results and discussion

Regarding the effect of the electrode composition, the three anodes produce a recovery of porosity of 100%. However, the Ti/RuO_2 anode produces the full regeneration of the AC in 1h, whereas longer times are necessary for the Ti/IrO_2 anode. The Pt/Ti anode is also efficient for the regeneration although it results in a higher cell voltage. On the other hand, electrochemical regeneration, in the same experimental conditions, is more efficient with increasing the electrolyte flow rate. Thus, the higher the electrolyte flow the higher the recovery of the porosity. A recovery of surface area of 85, 87, 93 and 96% is reached after 4h of treatment with increasing the flow rate. The desorbed compounds from the spent AC remain in the electrolyte.

Conclusions

The electrochemical regeneration is an efficient method for the regeneration of 15kg of spent AC and could be a real alternative to thermal methods at an industrial level.

Acknowledgements

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P17

Electrochemical regeneration of spent activated carbons used in different industries

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Introduction

Electrochemical regeneration of spent activated carbons (AC) can be considered as an eco-friendlier alternative to the common thermal regeneration [1]. With this methodology, a better recovery of the textural properties of the activated carbons are obtained and it can be used on-site, decreasing costs and CO_2 emissions [2]. Considering the variety of industries that use AC to control pollutant emissions, it is expected that the regeneration will be strongly influenced by the specific application of the AC. Here we present the study of the electrochemical regeneration of AC collected from a vapor recovery unit (VRU) from fuel processing industry and from a chemical industry that produces aniline (ANI).

Experimental

The samples were submitted to different electrochemical regeneration processes at lab-scale using an electrochemical filter-press cell, by changing operational variables as electrolyte and intensity of current applied. The AC samples were characterized by N_2 adsorption isotherms at 77 K, while the electrolyte was characterized by UV-Vis spectroscopy and Total Organic Carbon analysis (TOC).

Results and discussion

The characterization of the AC shows the optimal recovery of the porosity of VRU samples when they are submitted to a cathodic treatment in acidic media, leading to the desorption of the organic compounds. For the ANI samples, the best results are obtained for an anodic treatment, which leads to the oxidation/degradation of the monomer. The characterization of the electrolyte corroborates the presence of the desorbed species.

Conclusions

The recovery of the porosity of AC samples collected from two different industries has been successfully achieved. The source of samples becomes a key factor for the selection of the operational variables used during the treatment, due to the nature of the adsorbed species.

Acknowledgements

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P18

Graphene oxide nanofibers: synthesis and electrochemical properties

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Introduction

Graphene-based materials are very attractive for numerous applications such as electronics, sensors, energy-storage materials, composites or catalytic supports. Among the routes for the synthesis of these materials, obtaining them from graphitic carbon using chemical routes followed by ultrasonic exfoliation allows scalable processing in liquid suspension. Carbon nanofilaments can be used for graphene preparation as an alternative to the use of synthetic graphite [1], whose environmental sustainability and cost are penalized by the use of coke from petroleum processing and graphitization treatment at high temperature (> 2500 °C), respectively. In this work, fishbone carbon nanofibers (CNF) were subjected to different oxidation ratios (OR = $KMnO_4$/CNF) and ultrasound assisted exfoliation (1 or 2 h) to obtain graphene oxide nanofibers (GONF, Figure 1a), i.e. filamentous-like structures with ca. 0.75 nm interlayer spacing. The different levels of exfoliation and surface chemistry are key in their tunable electrochemical behaviour it terms of capacitance.

Results and discussion

Figure 1b shows the electrical capacitance vs potential curves of the as-synthesized CNF and the oxidized CNF, either by nitric acid or after the aforementioned oxidation/exfoliation processes (labeled according to the OR and the time of sonication used). All the oxidized/exfoliated materials presented a higher capacitance than the bare CNF due to the intercalation of O and S species, which increases the hydrophilicity of the material and hence, enhance the wettability by the electrolyte (0.5 M H_2SO_4). Interestingly, the sample treated under mild conditions (OR = 6, 1h) showed the highest values of capacitance, including a clear pseudocapacitive contribution, which may be explained by its mixed structure, between single nanofilaments and isolated graphene sheets, and the presence of surface O groups.

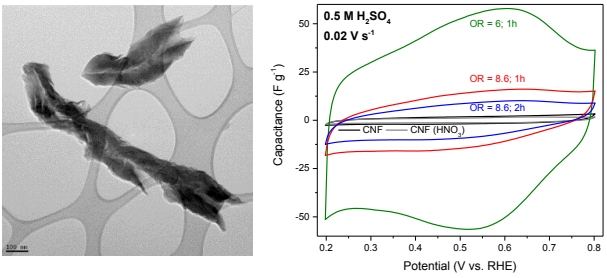

Figure 1. a) TEM image of GONF-OR=6-1h;
b) Capacitance vs potential curves of the carbon materials in 0.5 M H_2SO_4 aqueous solution, scan rate 0.02 V s^{-1}.

Acknowledgements

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P19

Activation and Functionalization of Expanded Graphite Electrodes to Promote Geobacter Activity in MFCs

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Introduction

Carbon materials play a key role as electrodes in the so-called Microbial Electrochemical Technologies to exchange electrons with electroactive microorganisms [1]. Particularly, expanded graphite (EG) electrodes gather several advantages for their utilization in microbial fuel cells (MFCs), but their low microbial electroactivity make them practically useful only as current collectors. In this work, the activation and functionalization of two types of EGs has been studied.

Experimental

The activation was carried out by CO_2 treatment at different temperatures (600-900 ºC) and for different times (4-12 h). Next, some activated samples were treated with boiling 65% HNO_3 to introduce surface oxygen functionalities. The materials were characterized by gas adsorption, Raman, XRD, TPD and XPS. Their microbial electroactivity was studied by CV and chronoamperometry in the presence and absence of Geobacter sulfurreducens and/or acetate metabolite.

Results and discussion

CO_2 activation treatment greatly develops the porosity of the PV15 electrode up to specific surface areas of ca. 110 m^2/g. As shown in the figure, the electric charge that can be adsorbed in the activated electrodes greatly increase. When polarized at 0.2 V (vs. Ag/AgCl/Cl^-) in the presence of Geobacter sulfurreducens and acetate, it has been observed that the introduction of micro and mesoporosity on PV15 remarkably enhances its biofilm activity, giving rise to up to 60 times higher steady-state currents.

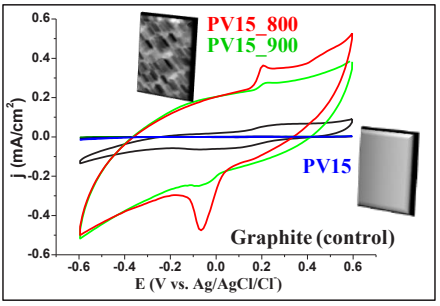

Figure. Stabilized cyclic voltammograms of different materials in fresh water medium before inoculation; v = 10 mV/s.

Conclusions

Nano-porosity and/or -roughness resulting from activation treatments greatly promotes the activity of Geobacter biofilms, so activated EGs become promising electrodes for MFCs.

Acknowledgements

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P20

N-doped holey graphene as a platform for efficient anode materials of Li-ion batteries

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Introduction

Doping of graphene layers with nitrogen is a way to increase the electrochemical capacity of the material via the creation of additional adsorption sites and change of its electrical conductivity. Nitrogen is embedded in the graphene lattice in various forms (pyridinic, graphitic, pyrrolic and NH_2), which affect differently the processes in Li-ion batteries (LIB). Creation of defects in graphene layer can allow nitrogen easier and in more amount to be incorporated in the lattice. In our work, we investigated the effect of the holes in graphene layers on nitrogen doping and used holey graphene (HG) and nitrogen-doped HG (N-HG) for deposition of MoS_2. The samples were comparatively studied by XPS and electrochemical impedance spectroscopy (EIS) and tested in Li-ion half-cells.

Experimental

For the creation of holes in graphene layers, graphite oxide was boiled in concentrated H_2SO_4 at 200 and 280°C (HG200 and HG280 samples). The products contain multiple nanoscale holes [1]. Doping of HG200 and HG280 samples was carried out by heating in an ammonia solution at 80 °C. The obtained NHG200 and NHG280 samples were annealed at 400°C in an argon flow for removal of oxygen groups (NHG200-400 and NHG280-400 samples). MoS_2 coating was formed by thermal decomposition of a MoS_3/HG mixture in pressing mould at 400 °C and 100 bar.

Results and discussion

XPS study revealed 4–5 at% of the nitrogen in NHG200 and NHG280. Analysis of N 1s spectra determined pyridinic, pyrrolic and amino groups. Hence, nitrogen predominantly binds along the graphene edges by replacing neighboring carbonyl groups. The NHG280-400 sample with a larger amount of pyridinic groups (=N-) had better performance (475 mAh g^{-1} at current density 0.1 A g^{-1}) as compared to the NHG200 sample (310 mAh g^{-1}), which was enriched by pyrrolic groups (-NH-). According to the EIS modeling, pyridinic nitrogen improves the ionic conductivity of the material. Testing of MoS_2/NHG200-400 and MoS_2/NHG280-400 hybrids showed that they have similar capacity values 680 and 625 mAh g^{-1} at 0.1 A g^{-1} for, respectively. It indicates that both pyrrolic and pyridinic nitrogen stabilizes MoS_2.

Conclusions

In summary, we showed that the presence of holes in graphene layers made it possible to introduce nitrogen in predominantly pyridinic and pyrrolic forms, which provide stabilization MoS_2 on nitrogen-doped HG. Pyridinic nitrogen in HG lattice increases ionic conductivity in LIB.

Acknowledgments

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P21

Impact of fluorination degree on sensor behavior of graphene film

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Introduction

Graphene has been kept the key place as a platform for gas sensor due to possibility to tune electronic and structural properties via covalent modification. Unsaturated carbon-carbon bonds in graphene are available for modification with functional groups, which allow to tailor electronic properties in wide range [1], improve reactivity of graphene and change its charge state [2]. Depending on the type of functional group it is possible to manage charge transfer in adsorbate/adsorbent system, adsorption equilibrium and interaction energy. However, in the efficient sensors, such interaction should not be too strong to provide an easy desorption of molecules. Here, we investigated sensor properties of fluorinated graphenes towards nitrogen dioxide depending on the functional composition at different temperatures in order to evaluate impact of fluoride groups on the kinetic behavior and the adsorption energy.

Experimental

Fluorinated graphites were obtained using gas phase fluorination of natural graphite in the BrF_3/Br_2 media. The fluorination degree was varied from $CF_{0.1}$ to $CF_{0.5}$ by the reaction time and concentration of fluorination agent. Fluorinated graphene was obtained liquid phase exfoliation of fluorinated graphite in toluene. The materials were characterized using scanning electron microscopy, Raman and X-ray photoelectron spectroscopy. The sensor properties were tested in the flow reactor at temperatures from 25 to 100 °C towards low concentration of nitrogen dioxide.

Results and discussion

The sensor response/recovery data indicates that type of chemical modification plays important role in the kinetics of analyte adsorption on the graphene surface. Fluorinated graphene (FG) can spontaneously recover to their initial states by air purging, without heating or vacuum pumping. The concentration of fluorine improves sensor performance of the FG films, which could be attributed with modification of electronic structure via fluorination and change of average adsorption energy of material. DFT calculations on the interaction of NO_2 with modified graphene surface explain change in the adsorption energy depending on the concentration and pattern of fluorine. The calculations show weak van der Waals interactions of the molecule with the fluoride groups on the graphene surface.

Conclusions

Our results show that fluorinated graphene is perspective for gas sensing at room temperature due to weak interactions with the NO_2 molecules and good kinetics. The sensitivity was determined from the relative response versus analyte concentration to be 0.2% ppm^{-1} and could be sufficiently improved by optimizing of geometry and thickness of sensitive layer.

Acknowledgements

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P22

Hybrid capacitor with anthraquinone grafted carbon operating in low pH aqueous salt solution as faradaic battery-like component

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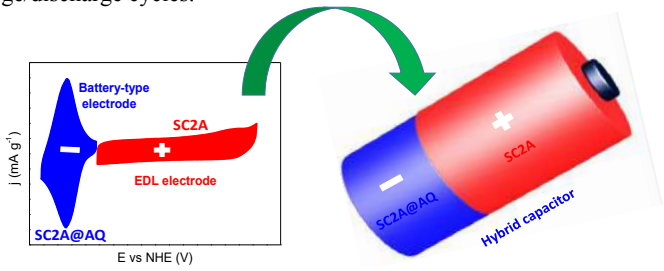
Hybrid capacitors combine one electrical double-layer electrode - usually a high surface area carbonaceous material, together with a faradaic battery-type component [1]. Recent examples of high conductivity battery-like electrodes are realized by operating carbon electrodes in a redox-active electrolyte [2] or by modifying carbon with electroactive molecules [3]. Grafted carbons, e.g., with anthraquinone (AQ) moieties, are recognized to display highly reversible redox activity in acidic electrolytes such as sulfuric acid, unlike in basic electrolytes where quinone-dianions are formed causing AQ detachment from the surface [3]. However, in H_2SO_4 electrolyte, expensive gold current collectors are required to avoid corrosion issues, and the operational voltage of carbon-based capacitors is restricted (~ 1V).

In the present study, anthraquinone (AQ) moieties (0.1eq. vs. carbon) have been grafted using the corresponding diazonium salts on the surface of the SC2A carbon black (Cabot, S_{DFT} =1502 $m^2\ g^{-1}$, total pore volume = 1.05 $cm^3 \cdot g^{-1}$). The AQ mass loading in SC2A@AQ was ~15 wt% as determined by CV and TG analysis. The DFT specific surface area of SC2A@AQ was reduced to 191 $m^2\ g^{-1}$, and the total pore volume dropped to 0.46 $cm^3 \cdot g^{-1}$. Despite the large difference in S_{DFT} values of the materials, the EDL capacitance values of SC2A and SC2A@AQ electrodes in 1 mol L^{-1} $BeSO_4$ (pH = 2.1) were comparable, owing to the improved wettability of the latter material. The performance of a (-)SC2A@AQ//SC2A(+) hybrid capacitor in 1 mol L^{-1} $BeSO_4$ was characterized by a quasi-linear GC/GD profile and twice higher capacitance compared to the symmetric (-)SC2A//SC2A(+) cell. The hybrid capacitor demonstrated an excellent discharge capacitance (from 1.6 V) retention during cycling, with only 13 % loss after 10,000 charge/discharge cycles.



Scheme 1: Illustrative scheme of (-)SC2A@AQ//SC2A(+) hybrid EC in 1 mol L^{-1} $BeSO_4$ electrolyte. 2-electrode Swagelok assembly with reference electrode: negative battery-type and positive EDL electrodes.

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P23

Activated carbon monoliths from lignocellulosic biomass waste for electrochemical applications

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Introduction

Activated carbons monoliths (ACMs) have shown promising results as electrodes for supercapacitors, due to their high volumetric density and large porosity. However, they are usually, made by compressing the corresponding activated carbon in the presence of a binder, which usually implies a reduction of pore sizes due to partial blocking, or in less extent in absence of any type of additive by applying a very high pressure In this work, different binderless ACMs were prepared and tested for electrochemical applications.

Experimental

Cylindrical activated carbon disk were prepared from olive stone, Alcell® and Kraft lignin by chemical activation with H_3PO_4 by extrusion without any kind of binder. Activated carbon disk were activated under inert atmosphere at 700 ºC and washing with distilled water. N_2 and CO_2 adsorption, XPS and CO-CO_2 TPD techniques were used to characterize the carbon electrodes. Their electrochemical performances were evaluated by cyclic voltammetry and galvanostatic charge-discharge at different current densities, without using binder and conductive promoter.

Results and discussion

Figure 1 shows the activated carbon disks used in this work. Carbon electrodes presented pore size distributions in the micro and mesopore range, with high surfaces areas (c.a. 1500 m^2/g) and relatively high mesopore volume (0.35 cm^3/g). The bulk density of the monoliths is also very high (~1.1 g/cm^3 for ACM from Alcell lignin), with compressive strength of 7.6 MPa. The activated carbon disk from olive stones presents the highest specific capacitance, with approximately 217 F/g and 205 F/cm^3. The values of specific capacitances for these ACMs are comparable or even better than others reported in the literature with similar porosity, but their volumetric capacitances are considerably higher than the values obtained at similar conditions by other authors.

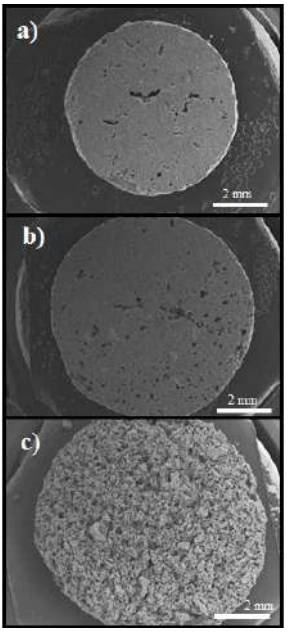

Figure 1. Activated carbon disk from: a) Olive stone; b) Alcell lignin; c) Kraft lignin.

Conclusions

Binderless ACMs from lignocellulosic waste were prepared by a simple preparation method from biomass waste precursors. These ACMs showed significantly high bulk densities and volumetric capacitances.

Acknowledgements

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P24

From Waste to Wealth: hardwood versus softwood Kraft lignin – porous electrospun carbon fibers via different thermal treatments

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Introduction

Kraft lignin has been the hopeful answer to the pressing question how to avoid or reduce the use of precursors from fossil reserves (e.g. hydrocarbons) in materials synthesis. Despite some success namely vanillin and DMSO from lignin the heterogeneity and complexity of Kraft lignin has often frustrated all hope.

Since lignin is not a well-established ("off-the-shelf ") chemical, but inherently a loosely defined precursor, it is crucial to characterize the lignin used as precursor to understand its structural and chemical features. In this work we compare two Kraft lignins with regard to their performance in aqueous supercapacitors.

Experimental

A pine-spruce softwood mixture (SKL) and eucalyptus hardwood Kraft lignin (HKL) were obtained from the LignoBoost process at RISE Innventia AB. After isolation both lignins were fractionated by sequential solvent extraction. Dissolved in DMF and methanol/DMF mixtures the lignins were electrospun. The as-spun lignin nanofiber mats were then converted to carbon nanofiber mats via stabilization at 250, 280, 310, 340 °C in air and carbonization at 800 °C in N_2. Afterwards, the materials were tested as free-standing supercapacitor electrodes in 6M KOH.

Results and discussion

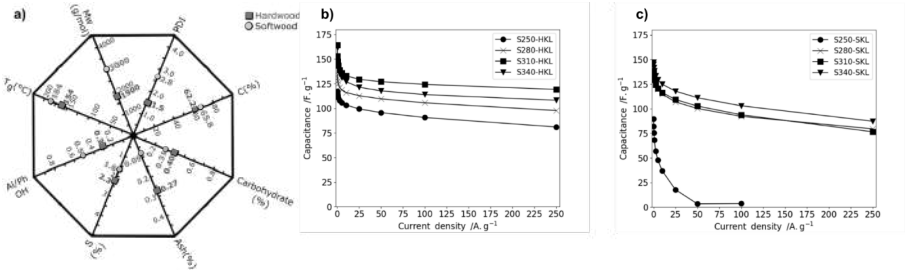

Figure 3 a) lignin property polygon**,** and capacitance versus current density for **b)** hardwood and **c)** softwood Kraft lignin.

Conclusions

The less condensed hardwood Kraft lignin shows improved performance compared to softwood Kraft lignin in alkaline electrolyte (6M KOH) based supercapacitors. Optimum performance was achieved with a stabilization temperature of 310 °C.

P25

Encapsulation of polyiodides in carbon porosity for hybrid electrochemical capacitors in aqueous electrolyte

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Commercially available electrochemical capacitors (ECs) with activated carbon (AC) as electrode material, either based on organic electrolyte ($TEABF_4$ in acetonitrile) or aqueous electrolytes (KOH and H_2SO_4), are able to operate at high temperature, e.g., up to 70°C [1-2]. However, due to the relatively high cost and environmental unfriendly character of organic electrolytes, and the limited voltage of 0.7-0.8 V when using basic (KOH) solutions, alternative electrolytes are desirable. Recently, voltage values as high as 1.5 V have been demonstrated with neutral aqueous electrolytes, e.g., lithium sulphate (Li_2SO_4), yet excessive gas evolution was observed at temperature higher than 40°C [3]. Besides, freezing at relatively high temperature represent an important disadvantage of neutral aqueous electrolytes. Recently, it has been shown that carbon/carbon hybrid electrochemical capacitors using bifunctional redox aqueous electrolyte based on the carbon/iodine interface can reach the performance of cells implementing organic electrolyte. Here, we introduce a new family of concentrated aqueous electrolytes based on choline nitrate ($ChNO_3$) or choline chloride (ChCl) as supporting neutral electrolyte and choline iodide (ChI), as redox active component, in which hybrid capacitors demonstrate excellent performance from +60°C down to -40°C [4]. Importantly, this electrolyte does not freeze at -150°C as identified by differential scanning calorimetry. Due to the confinement of polyiodides in carbon porosity (proved by TPD and Raman spectroscopy), the positive electrode exhibits a battery-type behavior, whereas the negative electrode is a typical electrical double-layer one [5]. The presentation will detail the performance metrics of prototype pouch cells in aqueous $ChNO_3$/ChCl + ChI from +60°C down to -40°C and show values comparable to those attained by capacitors made with the same carbon electrodes in organic electrolyte.

Acknowledgements

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P26

Activated carbons prepared through activation of biomass with H_3PO_4: Applicability as electrodes of electrochemical capacitors

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Introduction

One of the main challenges in the production of supercapacitors is the development of greener and cheaper carbon electrodes, avoiding expensive and time consuming purification processes. The hydrothermal carbonization method (HTC) is effective to produce activated carbons (ACs) from biomass waste, being friendly with the environment by involving renewable resources [1]. In addition, it has been proven that post-chemical functionalization treatments of ACs with nitrogen can improve their performance as supercapacitor electrodes [2]. In this work, we propose the synthesis of carbon electrodes by combination of hydrothermal carbonization and activation with H_3PO_4 of biomass waste with chemical post-functionalization treatments.

Experimental

Several ACs were submitted to N-chemical functionalization under mild conditions as reported elsewhere [2]. The ACs were synthesized by HTC in presence of H_3PO_4 and subsequent thermal treatment at different temperatures (450-900 ºC) [1]. A pristine commercial AC (WV-A1100) and after heat treatment at 900 ºC were also studied for comparison purposes. The carbon materials were characterized by XPS, temperature programmed desorption, cyclic voltammetry and galvanostatic charge-discharge cycles.

Results and discussion

N-functionalization of the carbon materials was achieved with similar content (1.6 - 1.9 at. % XPS) in form of different functional groups. These materials were employed as electrodes for symmetric supercapacitors in H_2SO_4 1M. The ACs obtained at low temperature showed poor electrochemical performance due to their lower conductivity and poor aromatic degree. The attachment of nitrogen groups in these materials did not improve the electrochemical behavior due to the formation of amines, which are detrimental for the electrochemical stability. However, the N-functionalization treatments produced on ACs obtained at high temperatures improved the performance, showing an enhancement of the electrochemical stability, energy efficiency and power density. This is related to the formation of N-heterocycles (pyrroles/pyridines and pyridines), that provide higher electrochemical stability, avoiding the formation of detrimental oxygen groups during the operation of the supercapacitor.

Conclusions

Post-functionalization treatments improved the electrochemical stability of low cost biomass derived activated carbons due to the beneficial effect of N-heterocycles.

Acknowledgements

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P27

Double layer formation of ionic liquids on different carbon surfaces

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Introduction

Ionic liquids are attractive electrolytes for supercapacitors due to their large theoretical voltage windows that allows to foreseen higher energy densities [1]. Nonetheless, their interaction with the surface of the carbon materials used as electrodes, and how these interactions influence the electrochemical performance of the SC, is not well understood [2]. This study intends to understand how the structure of the individual cations and anions of the ILs influences the formation of the electrical double layer on carbon electrodes with different areas, pore size distribution and surface chemistry.

Experimental

Symmetric cells with ILs (EMITFSI, EMIBF4) as electrolyte and different electrode materials (templated mesoporous carbon and microporous chemically activated carbon) were studied using synchronous chronoamperometric tests. The capacitance and energy efficiency of each IL/carbon and the overall cell are determined.

Results and discussion

Higher capacitance and energy efficiency are obtained in both symmetric systems that use the activated carbon as electrode, due to its larger surface area and large enough pores to accommodate the ILs ions. The asymmetric behavior between anode and cathode observed for EMITFSI/Mesoporous carbon evidences different interactions between the ions and the carbon surface. This interesting result will be further investigated. Additionally, the information will be used to build asymmetric systems with optimized performance.

Table 1. Capacitance and energy efficiency of symmetric systems.

	Mesoporous carbon (MC)				Activated carbon (AC)			
	Ĉ celda (F/g)	**Ĉ + (F/g)**	**Ĉ - (F/g)**	**Ê celda (W·h/kg)**	**Ĉ celda (F/g)**	**Ĉ + (F/g)**	**Ĉ - (F/g)**	**Ê celda (W·h/kg)**
EMITFSI	35	189	112	44	43	178	160	53
EMIBF4	34	141	136	43	50	202	196	62

Acknowledgements

The authors acknowledge Ministerio de Ciencia, Innovación y Universidades for financial support (project MAT2016-77114-R and the predoctoral contract of Noemí Quintanal, BES-2017-082038).

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P28

Improvement of the Performance of Superactivated carbon-based Electrochemical Capacitors by Adsorption of Metallacarboranes

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Introduction

Activated carbons (ACs) have been extensively employed as electrodes for supercapacitors. However, they experience degradation under high-voltage operation conditions. Among all the strategies for improving their electrochemical stability, the use of metallacarboranes (MCs) as mediators for hindering the degradation of carbon materials has appeared as a novel strategy for boosting the voltage of capacitors working in aqueous electrolyte (> 2V) [1]. In this work, we report the performance of supercapacitors based on superporous AC-containing MC in neutral aqueous electrolyte (0.5M Na_2SO_4) in presence of metallacarboranes.

Experimental

$Na[Co(C_2B_9Cl_2H_9)_2]$ MC and pristine AC were synthesized as reported elsewhere [1]. AC/MC mixtures were prepared by adsorption of MC solutions (in water) with different concentrations (0.015-0.080 M). The samples were characterized by N_2 adsorption/desorption at -196 ºC, XPS, cyclic voltammetry and galvanostatic charge-discharge cycles.

Results and discussion

MC was adsorbed on the activated carbon, as deduced from the increase in B content (0.9-5.8 % at. XPS) detected when increasing the concentration of MC in the solution. The adsorption of MCs resulted in a decrease of microporosity. These materials were used as electrodes for asymmetric supercapacitors (in mass). The cells based on AC-containing MC display high capacitance (36-43 F/g) and adequate coulombic efficiency (95-98 %), while the cell based on the unmodified carbon material shows poor coulombic efficiency (58%) due to the occurrence of faradaic processes that produce the degradation of the carbon material [1,2]. The durability of the devices was tested at high-voltage conditions (2V) to evaluate the effect of MCs. Under these conditions, the pristine AC-based capacitor shows poorer cyclability, while the electrodes modified with metallacarboranes display larger capacitance retention.

Conclusions

Aqueous-based supercapacitors were constructed using superporous ACs modified with MCs working at high voltage conditions. The devices showed large capacitance and excellent durability due to the stabilizing effect of MCs by its specific interaction with oxygen.

Acknowledgements

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P29

Low electrolyte diffusion on high surface area and spherical shaped activated carbons from bourbon waste

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Introduction

Bourbon whiskey production is very concentrated in the State of Kentucky, where 95% of the US production takes place. The production rate has increased nearly 300% in the last 20 years, for a total production of 7.5 million barrels per annum. As a distilled spirit, the non-distilled waste fraction supposes, per weight basis, 9 times more than the produced whiskey, which obviously had the same increase rate, and supposes nowadays a disposal problem. The bourbon waste is a thick slurry with solubles and insolubles, with a total solid content after evaporation between 6 and 10%, containing carbohydrates (mostly cellulose and some starch and derivates, 40%), lactid acid (20%), crude proteins (20%) and crude fat (20%).

It is well known that hydrothermal carbonization (HTC) of solved carbohydrates yields hydrochar, which may have perfect sphere shapes in the micron scale [1] and can be tailored in homogeneity and size when optimizing carbohydrate composition, concentration, temperature and time of treatment. This spherical hydrochar, among other applications, supposes a great raw material for supercapacitor electrode activated carbon [2]. At the same time, HTC is becoming one of the most attractive treatments of high-water content organic waste due to its high energy efficiency and neutral (even negative) CO2 footprint. Due to these reasons, HTC presents high interest in the bourbon industry since it can be an environmental and economic solution for their waste.

Experimental

Bourbon waste of a single distillery with 6% solids was used in this work. 3 HTC reactors of 300 mL, 2L and 10 L were also used, with times between 30 minutes and 5 hours. HTC of pure glucose and sucrose were used for comparison purposes. After HTC, hydrochar was filtered and dried. The hydrochar was subsequently carbonized at 500ºC for 30 min, then steam activated at 900ºC for various selective times to get activation burn-offs in the range 30-70%.

Results and discussion

Hydrochar yield in HTC was found to be the same (close to 50%) regardless treatment time, which does not happen when using solved sugars, and present microparticles of a nice spherical shape with minor irregular pieces. Resulting activated carbons were very microporous, which BET surface areas up to 1400 m2/g at 60% burn-off. Preliminary electrochemical measurements of the specific capacitance yielded very promising results, showing good performance at high scan rates (140 F/g), indicative of electrolyte high diffusion rate due to interspherical space.

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P30

Transitioning from binary PILs to zwitterionic-based ternary PILs to obtain liquid electrolytes at room temperature with enhanced electrochemical stability window

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Introduction

With a continuous increase of applications where ionic liquids can be used,[1] design of novel ILs offering "a la carte" properties is becoming a primary objective in many research fields. Under these circumstances and besides ILs containing novel compounds, double salt ionic liquids, eutectic mixtures of ILs, etc. are proliferating to face the challenge.[2, 3, 4]

Experimental

Herein, we describe the formation of ternary PILs from binary ones by the stoichiometric addition of a zwitterion.

Results and discussion

Addition of a zwitterion to a binary protic IL (PIL, formed between sulfonic acids and ethanolamine) resulted in the formation of a ternary PIL containing the original anion and cation, and the zwitterion acting as a "charge linker" between both ions. Interestingly, the resulting ternary PILs were liquid at room temperature despite the original PILs were not.

Conclusions

The liquid nature of this novel zwittwerionic-based ternary PILs not only allowed their use as electrolytes at room temperature but also a significant improvement in the electrochemical stability window, with a widening of the operational voltage of up to 3.9 V vs. Ag/AgCl in comparison with the original binary PIL.

Acknowledgements

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P31

Structure/function correlation of Na intercalation in hard carbons for sodium ion batteries

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Introduction

There is currently a great demand for high performing rechargeable batteries that at the moment can only be meet by the Lithium ion batteries (LIB). However, the available resources of Li and Co will not be able to meet future demands and alternatives must be developed. Sodium ion batteries (SIB) provide a promising candidate as it is cheap, abundant and much of the technology already in use for LIB can be readily used in SIB. But the use of SIB has so far been hindered by the lack of competitive anode materials as sodium does not intercalate into graphite, as such a safe and durable anode materials is necessary for SIB to compete with LIB.

Experimental

Carbon samples were made by the hydrothermal carbonization technique and used as anode electrodes in sodium ion batteries. The samples were studied using SAXS and total neutron scattering.

Results and discussion

One of the main candidates for SIB anode material is hard carbons (HC), an amorphous network of carbon mainly composed of disordered graphite like sheets of ~15 Å in size. These sheet are stacked in a "falling cards" fashion with an average distance of ~4 Å between sheets and little order in the orientation of adjacent sheets. HCs also exhibit significant micro-structure on the nano-scale(~1 nm), meso scale(100s nm) and micro-scale (μm). By synthesizing HC via hydrothermal carbonization the anode material can be easily manipulated by simply changing the precursor material to tailor the density of the nano and meso pores and by controlling the temperature the pore size and layer distance can be controlled. Here we show that this can be done without increasing the material cost and that the local structure is key to optimizing the electrochemical performance.

Acknowledgements

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P32

Iron-based carbon xerogels for metal-air batteries

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Introduction

Metal-air batteries (MABs) are foreseen as a new generation device aiming to replace Li-ion batteries (LIBs). MABs present a higher theoretical energy density, lower cost, environmental friendliness, and safety. In particular, iron-based materials are cheap and easily obtained, and so they can be used for both the negative electrode and the positive electrode in MABs [1]. Here, Fe-doped carbon xerogels were synthesized in order to be tested as both positive and negative electrodes of iron-air batteries.

Experimental

Materials were obtained from the polycondensation and pyrolysis of different mixtures of resorcinol, formaldehyde, silica and iron nitrate. The suitability of Fe-doped carbon xerogels (Fe-CXGs) as negative and positive electrode of an iron-air battery was assessed in a three-electrode cell in a 1M KOH solution, studying the redox reactions separately.

Results and discussion

Fe-CXGs was composed of magnetite (Fe_3O_4), maghemite (Fe_2O_3) and iron carbide (Fe_3C, cohenite). Figure 1 depicts a charge/discharge cycle of an Fe-CXG acting as negative electrode. The capacity is around 250 mAh/gFe at 0.4 V vs RHE (around 100 mAh/gFe at 0.1 V vs RHE). This is a low value for this application. The presence of Fe_3C in the composition could be preventing somehow the redox reactions for Fe_2O_3 and Fe_3O_4. The activity as bifunctional catalyst of Fe-CXGs as positive electrode is still under evaluation.

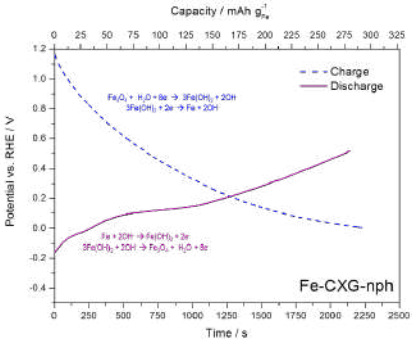

Figure 1. Charge/discharge cycle for an Fe-CXG acting as negative electrode of an IAB.

Conclusions

Fe-doped carbon xerogels were obtained and tested as iron electrodes for an iron-air battery. The capacity of these materials as iron electrode was not adequate, neither in terms of capacity nor in terms of potential.

Acknowledgements

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P33

Efficient Nickel-Based Catalysts Derived from a Metal-Organic Framework for Nitroarene Reduction

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Introduction

The development of highly active and selective catalysts is of great importance in many industrial processes and the preparation of alternative catalysts based on cheaper metals (e.g., Ni or Cu) the subject of intense research. The objective of this work was the preparation of Ni/carbon hybrid materials with a high catalytic activity.

Experimental

The catalysts were obtained by carbonization of an organometallic compound formed by coordination between nickel acetate and 2-methyl-imidazole. Samples are denoted as NiCx, where "x" is a number from 4 to 10 to indicate the carbonization temperature (400 to 1000 ºC). We tested the catalytic activity of these materials in the reduction reaction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) with NaBH4 as the reducing agent.

Results and discussion

As expected, both the size of the Ni nanoparticles (3, 7.5 and 37 nm) as well as the total metal content (45.5, 64.3 and 73.1 wt.%) increased with increasing the carbonization temperature (400, 700 and 1000 ºC, respectively). Focusing on the kinetics of the catalytic reaction, which exhibited a pseudo first order behaviour, a high apparent reaction rate constant (k') was measured for the Ni-carbon sample. In particular, the NiC4 sample exhibited the highest kinetic behaviour [k' = 0.186 $L \cdot g^{-1} \cdot s^{-1}$ (k'' = 0.410 $L \cdot gNi^{-1} \cdot s^{-1}$)]. A decreased kinetics was observed for samples NiC5 and NiC6. However, it increased for sample NiC7 and then decreased again for samples NiC8, NiC9 and NiC10.

Thus, two linear tendencies were noticed for the reaction kinetics as a function of carbonization temperature. Increment of the nanoparticle size does not explain this behavior. After an extensive characterization the explanation was obtained from the X-ray diffraction studies. NiC4 sample shows a peak at 44.75º was identified as rhombohedral Ni_3C. Samples NiC5 and NiC6, as well as the peaks at 44.45, 51.80 and 76.30º, which correspond to the face centered cubic (fcc) structure of Ni, they show two other peaks centred at 41.90 and 47.60º associated with an intermediate phase in the decomposition from rhombohedral Ni_3C (where carbon adopts the inside atom-positions in the structure) to fcc-Ni where nickel atoms could be forced to adopt a crystalline hexagonal close packed (hcp) form. In NiC7, residual hcp-Ni appears as a shoulder, whereas beyond 800 ºC only the fcc-Ni structure is observed in the diffractograms. Therefore, the two tendencies observed in the reaction kinetics may be due to the different catalytic activity of the nickel nanoparticles with different crystalline structure.

Conclusions

In this work, we have reported a simple method to prepare a highly active nickel-carbon catalyst by simple carbonization of an organometallic compound containing Ni and 2mIm as the ligand. These materials exhibited a very high catalytic activity in the reduction of 4-nitrophenol with $NaBH_4$. We have also discussed the possible effects of the Ni crystalline phase on the measured reduction kinetics.

Acknowledgements

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P34

Structure-Performance Correlations in Hard Carbons for Sodium-ion Batteries

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Introduction

Inexpensive, efficient energy storage systems are essential for the wide-scale successful implementation of renewable energy technologies. Among the various available energy storage technologies, Li-ion batteries (LIB) have been have received considerable attention. However, in terms of largescale application they are not suitable because their price is very high, which is resulting from the uneven distribution of lithium reserve around the world and increasing consumption. Hence, it is crucial to research low-cost secondary batteries for energy storage technologies. Sodium is located below Li in the periodic table, so it possesses similar chemical and physical properties to Li in many aspects. First of all, regarding availability sodium is fourth most abundant element in the Earth's crust, making sodium relatively inexpensive.[1-6] Namely, sodium-based batteries could provide an alternative chemistry to lithium batteries, and might become competitive to lithium-ion batteries. However, there are still inevitable drawbacks related to discovery of suitable anode materials. Optimizing the porous and graphitic structure of the anode materials is important to achieve electrochemically elevated Na-ion battery technology.

Experimental

In this study, we will present the preparation of a series of hard carbon anode materials prepared via the Hydrothermal Carbonisation (HTC) followed by high temperature carbonisation. Applying various carbon precursors, carbonization temperatures, templating agents and dopants results in materials with different pore morphologies, functional groups and graphitisation degrees which were characterised by HRTEM, XPS, Raman and SAXS. The influence of material morphology, type of the dopant and change microstructure on electrochemical performance and Na-storage mechanism were investigated by Galvanostatic Intermittent Titration Technique (GITT) and Electrochemical Dilatometry.

Results and Conclusions

In conclusion, we studied the effect of the carbonisation temperature on the storage mechanism and electrochemical performance of hard carbons obtained via HTC of glucose with citric acid. The Na storage mechanism can be correlated with the pore structure and degree of graphitisation.

Acknowledgements

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P35

Synthesis of nitrogen doped porous carbon–carbon nanotube hybrids for electrochemical applications

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Introduction

Various carbon materials, due to their availability, are the most promising and convenient for use as electrode materials for supercapacitors and Li-ion/Na-ion batteries. Typical values of surface area range from 120 to 500 m^2/g with specific capacity values from 2 to 500 F/g when using CNTs as the electrode material [1]. Making of hybrid materials can improve capacity of carbon based electrodes. There are two ways to perform this such as mechanical mixing of components or CVD synthesis of material.

Experimental

Polyoxomolybdate clusters such as $[Mo_{12}O_{28}(\mu_2\text{-}OH)_{12}\{\mathbf{Co(or\ Ni)}(H_2O)_3\}_4]$ and $[H_4Mo_{72}Fe_{30}O_{254}(CH_3COO)_{10}\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8(H_2O)\}_3(H_2O)_{87}]\cdot 80H_2O$ were used as catalyst precursors for CCVD synthesis of nitrogen doped porous carbon–carbon nanotube hybrid materials. The catalysts were prepared by impregnation and combustion methods. Carbon materials were synthesized by decomposition of reaction mixture of $CH_4/H_2/CH_3CN$ under catalyst at constant or dynamic temperature profile of CVD process. Supercapacitive performance of carbon materials was tested by three-electrode cell using «Bio-Logic SP-300». Two-electrode cells of the form factor CR 2032 were constructed with carbon materials and Li/Na metals to test charge-discharge processes using «Neware BTS-3000» station.

Results and discussion

The peculiarity of the present work is using cluster molecules which content Co, Ni and Fe with Mo. This type catalyst precursors with identical structure allows to estimate correctly influence of different metals on CNT structure. In the present work we demonstrated structure of carbon nanotubes to depend on method of catalysts preparation. It was shown that nitrogen doped porous carbon–carbon nanotube hybrids have an advantages over CNTs and nitrogen-doped CNTs.

Conclusions

It was found that the hybrid materials nitrogen doped porous carbon–carbon nanotube are more efficient than CNT and nitrogen-doped carbon nanotubes for electrochemical applications.

Acknowledgements

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P36

Sb/C hybrid materials for Na-ion batteries: the impact of carbon characteristics on Sb nanoparticles formation and electrochemical performances

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Introduction

During the last years, Na-ion batteries gain a lot of attention because of the sodium environmentally friendly nature and its high natural abundance compared to lithium.
In this work we report a facile synthesis of carbon based on eco-friendly bio-polymers followed by a ball milling procedure to prepare carbon materials doped with Sb NPs as anodes for Na-ion batteries. A systematic study was performed in order to understand the influence of carbon porosity, structure and surface chemistry on the Sb particle size/dispersion along with their electrochemical performances.

Experimental

A fast and facile ball milling procedure involving carbon materials obtained by soft-template methods and antimony salt followed by thermal reduction was implemented in order to obtain C/Sb nanocomposites. The influence of carbon texture, structure and surface chemistry on the Sb particle size/dispersion was evaluated by several techniques along with their electrochemical performances.

Results and discussion

The structural and morphological analysis indicate the formation of carbon-based materials with low degree of graphitization and uniform distribution of small size Sb NPs in the carbon matrix. The textural properties evaluated by N_2 adsorption indicate two type of materials: non- and mesoporous, with different specific surface area. The mesoporous C/Sb anodes tested for Na-ion batteries exhibit high reversible capacity after the first charge-discharge cycle of 639 mAh g^{-1} and a capacity retention of 224 mAh g^{-1}after 100 cycles. Regarding the non-porous C/Sb materials, the reversible capacity after the first cycle reaches 535 mAh g^{-1} with higher stability after 100 cycles than for mesoporous materials of 377 mAh g^{-1}. Moreover, irreversible capacity was successfully reduced by using carbon support with low porosity, surface area and surface chemistry.

Conclusions

Carbon based on eco-friendly precursors presenting different structure and porosity was used as support for Sb NPs. Carbons possessing higher surface area and larger amount of functional groups lead to smaller and better dispersed Sb NPs and improved electrochemical performances.

Acknowledgements

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P37

Doped Carbon Xerogels for Lithium/Sodium-ion Battery Anodes

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Introduction

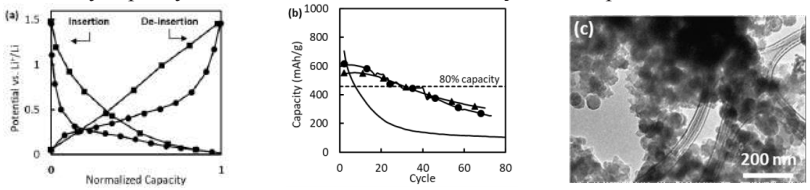
The use of dopants such as silicon, tin, and, more recently, antimony in carbonaceous anodes is a promising area of research to increase the performance of lithium and sodium ion batteries [1-3]. The biggest obstacle to the progress of this technology is the stability of these inclusions in the carbon material during charging and discharging, most notably the volume change of the active material [4-8].

Experimental

An electrode design was synthesized that consists of a carbon xerogel via a sol-gel process (CX), which acts as a support structure for a dopant, silicon nanoparticles (SiNPs), and provides electronic conductivity for a lithium/sodium-ion battery anode. Syntheses have been made using poly(sodium 4-styrenesulfonate) (PSS) as a coating or binder as a protective additive.

Results and discussion

A 5-fold increase was observed in the number of charge/discharge cycles before the reversible capacity was less than 80% the initial capacity when compared with a composite with no coating and a conventional binder. The gradual loss in capacity in the coated composite is still unknown, but may be due to the interplay between SEI formation and the volume expansion of the SiNPs. These problems are now being addressed by various techniques to improve the chemical and mechanical stability, and tailoring the microporosity and mesoporosity to reduce the irreversibly capacity loss and increase the accessibility to the dopant material.



(a) Charge Discharge Profile of CX (■) and CX/SiNPs composite (●). (b) Cycle stability composite with a PVDF Binder (▬), PSS binder (▲), or PVDF binder with a PSS coating (●) (c) TEM micrograph of CX/SiNPs composite.

Conclusions

A novel synthesis technique was presented including the sol-gel preparation of a conductive carbon xerogel matrix with impregnated silicon nanoparticles. The use of PSS as a protective additive was found to have a positive impact on the cycle stability of the CX/SiNPs composite material for use as an anode in lithium/sodium-ion batteries. Further refinement is currently being conducted to address the persistent instability in the silicon nanoparticles by exploring other polymer additives and synthesis techniques of the CX/SiNPs composite.

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P38

Three-Layers Graphene Coated Aluminum Current Collector for Improving the Cathode Performance of Lithium Ion Batteries

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Introduction

Lithium ion batteries (LIBs) are a significant technology in today's global green energy and they are integral to advances in portable electronics, electric vehicles, and grid storage. Motivated by the graphene's appealing properties, a large number of publications have discussed their fascinating applications as active materials and a conductive filler in electrochemical energy-storage devices. No study so far has fully exploited the intrinsic properties of 2D materials, such as high electrical conductivity, high corrosion resistance, good coating ability, and flexibility, for industrial applications of CVD-grown large-area few-layer graphene in energy-storage devices.

Experimental

We coated electrodes with various numbers of graphene layers via the repeated transfer of graphene-coated thermal release tape onto an Al foil. We characterized the microstructure of graphene coated Al foils. We evaluated graphene coated Al foil as current collector for the cathode of the LIB.

Results and discussion

We demonstrate a facile and effective method to address the poor performance of currently available electrochemical energy-storage devices, by tuning the layers in CVD-grown large-area few-layered graphene. The coating of large-area triple-layer graphene on a current collector helped us decrease the internal resistance between the current collector and the active materials, protecting the underlying collector from corrosion, sustaining good adhesion strength between them, and facilitating effective thermal dissipation from active materials to the current collectors, thereby greatly improving both the power capability and cyclability of electrochemical energy-storage devices. By simply interfacing three-layered graphenes on the current collector, we achieved extremely large enhancement (ca. 175%) both in the cathodic capacity retention of lithium ion batteries even after 100 cycles. Importantly, interfacial graphene coated aluminum presents to enhanced volumetric energy density and electrochemical, more than of conventional current collectors.

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P39

Fe/N-doped carbon with a dendritic structure for use as efficient electrocatalyst in ORR

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Introduction

The commercialization of fuel cells is currently limited by the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode, which requires large amounts of costly and scarce Pt-based catalysts. Alternatively, low cost porous carbons doped with small amounts of noble metals show a good catalytic performance, but they need to meet several requirements such as a highly accessible porosity and small metal particle sizes. Herein we report the preparation of a new Fe−N−carbon material composed of nanoparticles with a dendritic morphology and uniformly distributed nitrogen and iron functional groups that exhibits a high ORR activity.

Experimental

A detailed description of the synthesis of the Fe−N−doped carbon nanopompoms can be found in [1]. Briefly, the silica templates were impregnated by a $FeCl_3$ ethanol solution and exposed to pyrrole vapor at 25 °C. The impregnated sample was carbonized at 600 °C and the silica template was removed with HF. Fe was incorporated by impregnating the resultant N-doped carbon with a solution of $FeCl_3$ in ethanol followed by carbonization to 800-900 °C.

Results and discussion

The Fe−N−C catalyst exhibits a dendritic pompom-like morphology (particles of ~240 nm) and an open mesoporous structure made up of interconnected carbon layers (S_{BET} ~500 $m^2\ g^{-1}$). It has a high content of nitrogen (~11 wt %) and iron coordinated to nitrogen (~5 wt %), that constitute numerous highly accessible active sites. The as-prepared Fe−N−C catalysts exhibits excellent activity with high onset potentials (0.94 V in 0.1 M KOH and 0.75 V in 0.1 $HClO_4$) and high selectivity towards the 4-electron process. Moreover, these Fe−N-doped carbon catalysts have better durability than commercial platinum in both media.

Conclusions

The novel Fe−N−C dendritic catalyst exhibits an excellent electrocatalytic activity in both acidic and basic media, and better long term stability than commercial platinum.

Acknowledgements

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P40

Biomass Based Activated Nitrogen Doped Carbons for Fuel Cells

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Introduction

The goal of this research is synthesis of nanoporous activated carbons with high specific surface on the base of wood charcoal and Kraft pulping residues, their structural modification with nitrogen, and determination of nitrogen content depending on synthesis conditions and carbonaceous precursor. The obtained carbons were tested as candidates for application as oxygen reduction (ORR) cathode in the low-temperature fuel cells.

Experimental

Alder wood char, cellulose, black liquor and fine cellulose sludge were used as precursors. Activated carbons (AC) were obtained using chemical activation method with NaOH at 700 ºC in argon. Nitrogen was introduced into AC using DCDA solution in DFA, doping was performed at 800 °C for 1 hour in argon. The following tests were performed: porosity, elemental compositions, XPS, Raman spectroscopy, RDE electrochemical measurements.

Results and discussion

It is demonstrated that content of introduced nitrogen depends on oxygen content in the structure of carbonaceous precursor. The ORR activity of the carbon materials in the case of activated doped wood char and black liquor was comparable with commercial 20% Pt/C catalyst. Electrocatalytic properties of the synthesized N-doped wood-derived carbon catalysts may be associated with the highly developed surface area, micro- and mesoporosity, as well as structural qualities of the biomass based carbon materials, high percentage of pyridinic nitrogen and lack of stacking defects of graphene layers.

Conclusions

The results of this study prove that nitrogen doped activated carbons on the base of biomass are promising materials for application in fuel elements for oxygen reduction.

Acknowledgements

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Palladium nanoparticles supported on carbon materials as cathode electrocatalyst in fuel cell

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Introduction

Energy conversion and generation have generated a great attention in the last decades in order to develop alternative technologies to replace the use of fossil fuels. Fuel cells and metal-air batteries can be considered as one of the most promising and clean new energy technologies. Unfortunately, high cost of the catalyst employed in this kind of the technology, especially in the cathode, restricts their proper commercialization. One alternative is the combination of carbon material supports, which possess high surface area and electrical conductivity, with metal nanoparticles in low loading, generating a nanostructured material which may improve the interaction and, consequently, the performance of these catalysts, due to the synergic effects between both components and the unique physical and chemical properties of the nanoparticles.

Experimental

In this study, palladium nanoparticles have been synthesized by the reduction-by-solvent method and have been loaded on a carbon support. The nanostructured Pd/carbon based catalysts were tested as cathode for ORR in alkaline medium

Results and discussion

The obtained catalysts gave excellent results in the rotating ring disk electrode for a Pd content lower than 3wt%. These materials have also been tested as cathode in a fuel cell station. Figure 1 shows the polarization and power curves using the Pd/C (0.075mg$_{Pd}$/cm^2) catalyst as cathode and Pt/C (0.5mg$_{Pt}$/cm^2) catalyst as anode. As the anion exchange membrane, a polysulfone membrane functionalized with an ammonium salt was used.

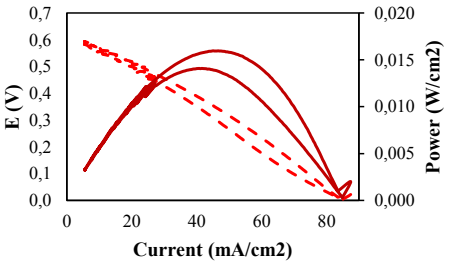

Figure 1. Polarization and power curves for a PEMFC in alkaline conditions using the Pd/C catalyst as cathode

Conclusions

The nanostructured Pd/carbon based catalysts were tested for ORR in alkaline medium an as cathode in a fuel cell station giving excellent results for a Pd content lower than 3wt%.

Acknowledgements

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P42

Titania-templated ordered n-doped mesoporous carbon thin films as highly efficient catalysts towards oxygen reduction reaction

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Introduction

Metal-free catalysts are one of the most promising alternatives as cathodes for oxygen reduction reaction (ORR) in fuel cells and metal-air batteries. Among them, N- doped carbon materials are one of the most studied. The most common preparation methods of N-doped carbon materials are based on the heat treatment of a mixture of nitrogen and carbon-containing precursors. The main problem of these routes is that the pore structure and size distribution cannot be controlled[1]. One possibility to control the structure of the materials is the use of a template. In this study, we report a method to synthesize N-doped mesoporous carbon thin films with high control over the N active sites towards ORR and pore distribution by electropolymerization and carbonization of a thin film of polyaniline on a mesoporous titania thin film template. Polyaniline is electropolymerized within the pore structure of titania template via chronoamperometry. The resultant samples were heat treated in order to obtain N-doped carbon materials with control over the pore structure and surface area.

Experimental

The electrochemical polymerization and characterization of the materials were performed in 0.1 M and 0.1 M H_2SO_4 solutions. The samples were characterized by XPS and TEM microscopy and the ORR activity was evaluated with LSV curves in O_2-saturated atmosphere.

Results and discussion

The titania ordered mesoporous structure was confirmed by TEM images. The extended characterization of the carbon materials after polyaniline carbonization, shows the presence of a high concentration of quaternary-type nitrogen species and it was also observed the formation of titania oxynitride species. Moreover, the higher the amount of polyaniline and heat treated, the higher the catalytic activity of the samples.

Conclusions

The presence of oxynitride species or the large amount of quaternary-type nitrogen species seems to be the responsible for the high catalytic activity of the 2D PANI-derived carbon materials with an excellent control over the pore structure and surface area.

Acknowledgements

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P43

Benzaldehyde production with scorpionate complexes immobilized in hydrochar supports

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Introduction

Oxidation reaction of styrene towards benzaldehyde is one of the most studied reactions due to the problems associated to the industrial processes used for the production of this valuable chemical. The development of a greener process for this transformation is needed, and different types of homogeneous catalysts have been heterogenized.

Experimental

For details on the synthesis and characterization of copper(II) C-homoscorpionates (1, 2,and 3), hydrochars (S0 and S10), immobilization, and catalytic assays are reported see ref. 1 and 2.

Results and discussion

Three different copper(II) C-homoscorpionates were tested in homogenous conditions showing excellent activity, i.e. 100% of selectivity and 68% of conversion after 5min in optimized conditions. Testing the immobilized scorpionate complexes in solvent-free conditions allowed to achieve 50% of conversion after only 2h of reaction, being benzaldehyde the major product. As recycling is the major advantage of these catalysts, the best performing material was tested and after the 4th catalytic cycle presented 50 % of the initial conversion but the selectivity to benzaldehyde remained unchanged (Figure 1).

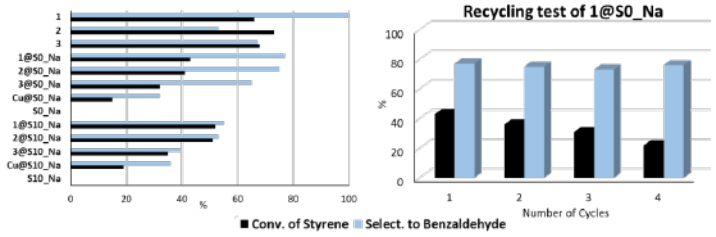

Figure 1. Results of homogeneous and heterogeneous tests.

Conclusions

Hydrochars can be used as catalytic supports of copper(II) C-homoscorpionate complexes to produce benzaldehyde under mild oxidation conditions, allowing the catalysts recycling.

Acknowledgements

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P44

Activated carbon of passion fruit biomass as support for $H_3PW_{12}O_{40}$

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Introduction

The present work had as objective to investigate the use of the lignocellulosic residue of the passion fruit seed in the preparation of activated charcoal for use as HPW support for application purposes in the esterification of oleic acid, a model reaction for the production of biodiesel from oily raw materials of high acidity.

Experimental

Activated carbon (CAM) was obtained from the passion fruit seed residue using as an activating agent ZnCl2 in a ratio of 1:1 (wt:wt). To obtain $H_3PW_{12}O_{40}$ (HPW) on the CAM support at different concentrations (10, 20 and 30 wt%), two procedures were used: aqueous impregnation and dry impregnation (incipient moisture), using HPW solutions in deionized water: ethanol (50:50 vol%: vol%). After each impregnation, the HPWx / CAM and HPWx / ICAM catalysts were dried and calcined.

Results and discussion

Analyzes of TG, FTIR, XRD, ^{13}C NMR, XPS and the adsorption of N_2, as well as SEM, confirmed the production of the activated carbon CAM, which presented high surface area (SBET = 465,5 m2 / g), and porous structure with predominance of micropores, after the process of pyrolysis of passion fruit biomass. The results of FTIR, XRD, ^{13}C NMR and XPS of the catalysts resulting from the aqueous impregnation and, similarly, impregnation via incipient moisture, of the HPW on the activated carbon carrier, showed an interaction between the active phase and the catalytic support in the concentrations of 10 to 30% by mass of HPW. More than 93% of the protons accessible to KOH were found in the acidity tests, for both methods of preparation. Thus, the results of the esterification tests showed that the catalysts containing the highest HPW increase (HPW30 / CAM and HPW30 / ICAM) showed good performance, achieving a conversion of more than 80%.

Conclusions

the results showed that the methodology was effective for the preparation of activated charcoal using the passion fruit seed and, likewise, the impregnation of HPW in this material, presenting a performance of 88% in the catalytic activity of the esterification of oleic acid in the presence of the composites HPW / CAM prepared for both methods.

Acknowledgements

The authors thank LabTecLim / UFPE, LAQIS / UFRPE and Servicios Centrales de Apoyo a la Investigación (SCAI) laboratories at University of Malaga and CNPq.

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P45

Kinetic study of dimethyl ether synthesis from methanol on Zr-loaded P-containing mesoporous activated carbon catalyst

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Introduction

Dimethyl ether (DME) is a potential renewable substitute for petroleum derivatives, such as liquefied petroleum gases (LPG) or diesel [1]. DME is produce via methanol dehydration on solid acid catalysis and we propose a biomass-derived acid carbon as a catalyst for this reaction.

Experimental

An activated carbon was prepared by chemical activation of olive stones with phosphoric acid followed by Zr loading (5% (w/w)). The methanol dehydration experiments were carried out in a fixed-bed reactor in the temperature range of 250-400 ºC, at different methanol partial pressures (0.02-0.08 atm), and space times (W/F_{MeOH}, 0.025-0.125 g·s/µmol).

Results and discussion

Three different kinetic mechanism for the selective methanol dehydration to DME have been proposed, with Zr-O-P type surface groups as catalytic active sites. The reaction seems to proceed through a modified Langmuir-Hinshelwood mechanism, in which two methanol molecules are subsequently adsorbed on one active site, with different adsorption enthalpies. The model reproduced the experimental data with a high accuracy (see Fig. 1). The activation energy for the DME production was calculated and a value of 70 kJ mol^{-1} was obtained.

$$-r = \frac{k_{sr}\left(K_{M,1}K_{M,2}P_M^2 - \frac{P_{DME}P_W}{K_{sr}K_W}\right)}{1 + K_{M,1}P_M + K_{M,1}K_{M,2}P_M^2 + \frac{P_W}{K_W}} \quad (Eq\ 1)$$

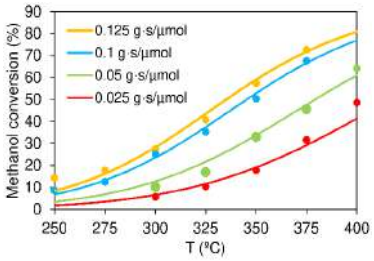

Fig. 1. Steady-state methanol conversion as a function of temperature

Conclusions

The Langmuir-Hinshelwood kinetic model that assumed two different methanol adsorptions reproduced the experimental data with high accuracy. The calculated activation energy is consistent with the data reported in bibliography.

Acknowledgements

MINECO (Project CTQ2015-68654-R) and MICINN (Project RTI2018-097555-B-100) for financial support. J.P. and M.A.R-C. also thank to Universidad de Málaga.

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P46

Palladium decorated nitrogen-containing carbon xerogels as efficient catalysts for the dehydrogenation of formic acid

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Introduction

Carbon materials have been extensively used as catalyst supports for the dehydrogenation of formic acid (FA) [1]. The incorporation of nitrogen groups has been claimed to be a useful tool to enhance the catalytic performance. Carbon xerogels are particularly interesting because their surface chemistry and porosity can be easily tuned [2, 3]. Herein, the effect of the pore texture and nitrogen content of catalysts based on Pd nanoparticles (NPs) supported on nitrogen-containing carbon xerogels (Pd/N-CXs) on the catalytic performance for the production of hydrogen from the dehydrogenation of FA was assessed.

Experimental

N-CXs were synthesized following a sol-gel protocol [3]. Supports were denoted as *a*N-CX-*b* (*a*, N wt.% and *b* meso- or macropores). Pd/N-CXs were prepared by a wet impregnation method to get a final Pd-loading of 0.5 wt.%. Several Pd/*a*N-CX-*b* catalysts with different pore textures (micro-mesoporous and micro-macroporous textures) and nitrogen contents (2-8 wt.%) were synthesized. Their catalytic activity at 75 ºC was evaluated in a burette system using an aqueous solution of HCOOH/HCOONa (9/1, 1M).

Results and discussion

TEM micrographs revealed that nitrogen content had an important effect on the Pd NPs size, obtaining average sizes around 3 nm in the case of catalysts with a moderate nitrogen doping. The time courses for the hydrogen production from FA indicated that the pore texture of the support played a key role in the catalytic ability, being the micro-mesoporous texture more suitable. The most active catalyst (Pd/4N-CX-meso) showed an initial TOF value of 2014 h^{-1}.

Conclusions

The results obtained for Pd/N-CXs demonstrated that the nitrogen functionalities influenced on Lewis basicity of the catalysts and the electronic features of the Pd species. Such aspects together with an adequate pore texture developed in the carbon xerogels resulted in enhanced performances for the FA dehydrogenation reaction.

Acknowledgements

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P47

Activated Carbon as acid catalyst for furfural valorization

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Introduction

The need for efficient use of resources will necessarily comprise biomass valorization. As a consequence, biomass obtained chemicals became more relevant in the chemical industry. Furfural is one of the platform molecules that can be easily obtain from biomass and from biomass waste. In order to achieve true sustainability not only the source of the materials has to be carefully chosen but also the total processes involved until final products. Circular economy demands a new look over the all life cycle. Researching new and sustainable transformation processes for the biobased chemicals becomes very relevant, and catalysis and catalysts a pivotal element of development. In this work we report the use of sustainable and environmental friendly carbon based catalysts in the transformation of furfural in the acetalization reaction.[1]

Experimental

Two series of modified porous carbons were prepared: i) N-N, CF-N, CZN and ii) N-S, CF-S. where N, CF, CZ denote the carbon support name (N-commercial Norit, CF- xerogel carbon from furfural [2]; CZ – ordered mesoporous carbon from self-assembly approach, using a soft template as a structure-directing agent [3] and N (HNO_3) or S (H_2SO_4) stand for the acidic treatment. The catalytic acetalizations were carried out at 60 ºC, when the mixture of 244 mg (0.8 mmol) of furfural, 0.250 ml of undecane (internal standard) and an excess of anhydrous ethanol (12 ml) reached 60 ºC, the addition of 200 mg of carbon catalyst started the reaction. Samples were periodically taken and analysed by GC.

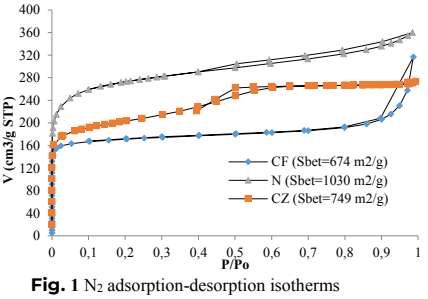

Fig. 1 N_2 adsorption-desorption isotherms

Results and discussion

All the carbon materials functionalized with acid sites were successfully tested in this reaction, yielding the diacetal in total selectivity and high conversion (almost 80 %, fig 2).

Conclusions

Almost no difference was observed between carbons, but the commercial carbon seems to present the lower performance.

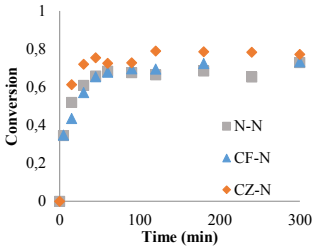

Fig. 2 Reaction of acetalization of furfural with ethanol in the presence of carbon catalysts

Acknowledgements

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P48

Functionalized mesoporous activated carbons as catalysts for cellulose hydrolysis

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Introduction

Biomass conversion into fuels and chemicals can contribute to reduce the world's dependence on fossil fuels, being lignocellulosic residues the most convenient feedstock. Cellulose, the most abundant component of lignocellulosic biomass, can be considered a suitable raw material, and hydrolysis an appropriate process to obtain important molecules, such as glucose or hydroxymethylfurfural [1]. The use of hydrolysis catalysts is necessary to enhance the degradation of the robust structure of cellulose. In this work, heterogeneous catalysts consisting of carbon materials functionalized by oxidation and sulfonation treatments at room temperature have been prepared, characterized in tested in the hydrolysis of cellulose.

Experimental

SA-30 commercial AC (MeadWesvaco), named SA, was treated either with a saturated solution of $(NH_4)_2S_2O_8$ in 1M H_2SO_4 (sample SAS) or only with 1M H_2SO_4 (sample SASu) (1 g activated carbon/10 ml solution, stirring, 24 h, room temperature). The Amberlyst-15 resin has been used as reference catalyst. The carbon catalysts have been thoroughly characterized by N_2 adsorption at -196ºC, XPS and TPD to analyse the oxygen functional groups (OFG). The catalytic tests were performed using 500 mg cellulose, 125 mg catalyst and 25 ml distilled water, at 190°C for 3 h, under stirring. The liquid phase was analysed by HPLC and the solid was dried and weighted to calculate the cellulose conversion.

Results and discussion

Table 1 shows the main properties of the prepared carbon catalysts.

Table 1. Textural properties and CO_2 and CO evolved in TPD measurements

Sample	S_{BET} (m^2g^{-1})	V_{meso} (cm^3g^{-1})	CO_2 (µmol/g)	CO (µmol/g)
SA	1464	0.73	1.40	3.83
SASu	1522	0.60	1.24	3.44
SAS	1274	0.48	0.99	3.11

OFG= CO + CO_2 from TPD

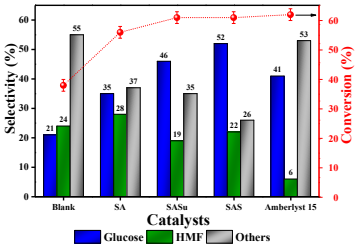

Fig. 1. Cellulose conversion (red points) and products selectivity →

The high specific surface area and well-developed porosity of SA carbon is only slightly modified after treatment with 1M H_2SO_4 (SASu sample), while it significantly decreases upon treatment with $(NH_4)_2S_2O_8$ in 1M H_2SO_4, SAS catalyst. Cellulose hydrolysis with the four tested catalysts renders, mainly, glucose and hydroxymethylfurfural (HMF) (Fig. 1). From the studied catalysts, SAS is the most effective, leading to 61% cellulose conversion and 52% selectivity to glucose. This good behaviour can be attributed to a proper combination of high OFG content and suitable porosity.

Acknowledgements

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P49

Carbon-supported Pd-Cu catalysts in nitrate reduction: the role of AOT surfactant on performance

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Introduction

Pollution of groundwater by nitrate due to anthropogenic activities has generated a growing environmental and human health risk. Catalytic reduction of nitrate to nitrogen with hydrogen has attracted attention as a method for drinking water production from polluted groundwater [1]. A main issue limiting applicability is side reactions producing ammonia. Former works [2,3] showed that Pd nanoparticles can be shielded using AOT (sodium bis-2-ethylhexyl sulphosuccinate) and used as catalysts highly selective to nitrogen in nitrite reduction. In this work this concept is extended to bimetallic catalysts and nitrate reduction.

Experimental

Bimetallic Pd-Cu and monometallic Pd and Cu catalysts were supported on activated carbon and tested in nitrate reduction in water ($C_{initial}$ = 100 ppm) using semi-batch reactors (H_2 and CO_2 flow). Catalysts were prepared by microemulsion using AOT as surfactant, and by incipient wetness impregnation (IWI) followed in some cases by exposure to AOT.

Results and discussion

Catalysts prepared by microemulsion and catalysts exposed to AOT after IWI synthesis showed lower activity in nitrate reduction than those prepared just by IWI, evidencing shielding of Pd active sites. However, shielding also prevented ammonium generation due to AOT interaction at low coordination sites. Experiments with bimetallic catalysts prepared by physically mixing Pd and Cu monometallic catalysts resulted in very low activity in nitrate reduction, which was ascribed to the interference of AOT in the Pd-Cu redox mechanism and lower hydrogen spillover. In spite of this interference, the catalysts maintained the ability to reduce nitrite in the second step of the reaction pathway with negligible production of ammonium.

Conclusions

Shielding of Pd sites by AOT during catalyst synthesis provides an effective way to avoid or significantly decrease ammonium formation in nitrate reduction. However, more research is required to achieve a better balance between activity in nitrate reduction and selectivity to ammonium.

Acknowledgements

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P50

Catalyst deactivation and regeneration for MTD reaction on Zr carbon-based catalyst

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Introduction

Dimethyl ether (DME) is a well-known diesel substitute. It can be obtained from methanol dehydration by using an acid catalyst, like γ-alumina, HPAs or activated carbon[1]. However, all of them suffer deactivation by coke deposition. Deactivation and regeneration of a Zr-loaded activated carbon were analyzed.

Experimental

Olive stone (OS) was activated with H_3PO_4 (H_3PO_4/OS ratio of 2:1) at 800ºC for 2 h. After washing, it was impregnated with $ZrO(NO_3)_2$ and treated at 250ºC for 2 h. Catalytic test was performed in a fixed bed reactor (space time of 75 $g_{cat}\cdot s/mmol_{CH3OH}$; methanol partial pressure of 0.04 atm; temperatures between 450 and 600ºC). Used samples were exposed to an air treatment at 350ºC for 2 h to assess its possible regeneration.

Results and discussion

onversion and selectivity remained high for more than 10 h, at temperatures as high as 550ºC. Catalytic activity seems to be related to surface zirconium phosphate. ss-^{31}P RMN results seem to indicate that zirconium hydrogenphosphate is the responsible of the long-term activity.

XPS analyses suggest that these active sites are partially covered by coke deposition, also reducing the porosity. Air treatment is not able to recover the initial porosity nor activity due to the presence of highly recalcitrant coke.

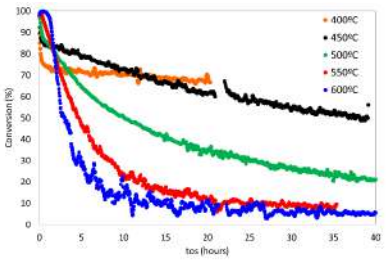

Fig. 1. MeOH conversion as a function of tos in fresh catalyst ($0.04\ atm_{MeOH}$, $75\ g_{cat}\cdot s/mmol_{MeOH}$)

Conclusion

The catalyst maintains a good yield to DME at high temperature, although a slow deactivation by coke deposition is detected and cannot be reverted by air treatment. It seems that zirconium hydrogenphosphate is the responsible of the long-term activity of this catalyst.

Acknowledgements

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P51

Efficient Ru/carbon catalysts prepared by pyrolysis of supported Ru complex for the hydrogen production from ammonia borane

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Introduction

Hydrogen carrier molecules have attracted great attention because they could palliate the important problems related to controlled H_2 storage and release. In this context, ammonia borane (NH_3-BH_3, AB) is considered a promising chemical H_2 storage material, attending to its high theoretical gravimetric H_2 content (19.6 wt.%), stability in solid state, non-toxicity, etc. This study is focused on the development of high-performing carbon-supported Ru catalysts towards the H_2 production from AB.

Experimental

Carbon-supported Ru catalysts were synthesized by an impregnation method using tri(2,2-bipyridyl) ruthenium (II) chloride hexahydrate and various decomposition temperatures (600-1000ºC) [1]. The as-synthesized Ru-based catalysts were denoted as Ru/C(T).

Results and discussion

Ruthenium nanoparticle (NP) size was dependent on the carbonization temperature and it ranged from 3.8 to 13.5 nm. Furthermore, the catalytic activity for H_2 generation from the hydrolysis of AB was directly related to the NPs size (see Figure 1). It was observed that the catalytic activity exhibited a volcano-type relationship with the NP size. The best-performing catalyst among investigated was Ru/C(800), achieving an average TOF of 670 mol H_2/mol$_{Ru}$ min. Moreover, the reusability of Ru/C(800) revealed that almost complete conversion of AB to H_2 was kept after five cycles, while TOF value decayed about 60% of the initial TOF in the 5th run.

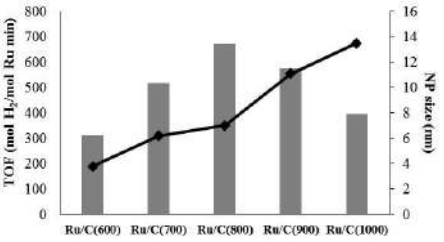

Figure 1. TOF number (t = 5.5 min) for the Ru/C samples and average NP size.

Conclusions

Highly efficient Ru/C catalysts towards the AB decomposition reaction have been successfully prepared by using $Ru(bpy)_3^{2+}$ as metal precursor. It is expected that this synthetic strategy can be extendable in the deposition of other metal catalysts.

Acknowledgements

The present work was partially supported by Grants-in-Aid for Scientific Research (Nos. 26220911, 25289289, and 26630409) from the Japan Society for the Promotion of Science (JSPS) and MEXT. MNG thanks JSPS for the Postdoctoral Fellowship (A17F173810).

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P52

Dehydrogenation of formic acid catalyzed by carbon-supported Pd catalysts: Investigation of size sensitivity

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Introduction

Formic acid (FA) is a stable liquid-phase chemical H_2 storage material, whose high gravimetric and volumetric hydrogen capacities, together with its non-toxicity make it a promising candidate. The use of Pd-based catalysts is one of the most favorable alternatives to boost the FA dehydrogenation [1]. In this work, we investigate the size sensitivity in the production of hydrogen from FA over carbon-supported PVP-capped Pd nanoparticles (NPs) by assessing the catalytic behavior of Pd/C catalysts with sizes ranging from 2.7 to 5.5 nm.

Experimental

Pd NPs were initially prepared in colloidal form by means of the polyol method. The fine control of the NP size was achieved by using different experimental conditions in terms of PVP/Pd molar ratio, reduction temperature and time, as well as metal precursor concentration. Pd/C catalysts were prepared with the as-synthetized colloids.

Results and discussion

The production of H_2 achieved after 3 h of reaction together with the NP size for the Pd/C catalysts is plotted in Figure 1. Sample Pd/C(3) (average particle size of 3.9 nm) exhibited the best catalytic performance, producing 183 µmol of H_2. Samples Pd/C(2), Pd/C(4) and Pd/C(5), showed similar H_2 evolution profiles and sample Pd/C(1) with the smallest NP size, displayed the poorest performance. Calculations on the Pd crystallites determined that this volcano type relationship between the catalytic activity and the Pd NP size was assigned to an optimum relative proportion of high-coordination sites in sample Pd/C(3) as compared to the other samples.

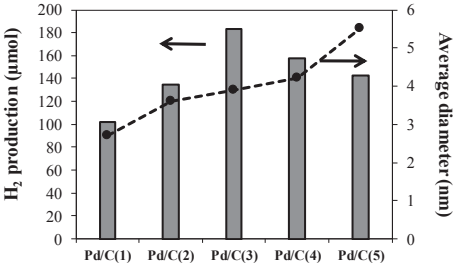

Figure 1. Relationship between H_2 production after 3 h of reaction at 30 ºC and the average NP size.

Conclusions

The results herein summarized reveal the importance of the NPs features towards the optimization of Pd-based catalysts for the H_2 production from FA decomposition.

Acknowledgements

MNG thanks the Japan Society for the Promotion of Science (JSPS, A17F173810 y J171015004) and the Generalitat Valenciana (project Plan GenT, CDEIGENT/2018/027) for the financial support.

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P53

Carbon-supported PdAg catalysts for the production of hydrogen from dehydrogenation of formic acid

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Introduction

Hydrogen is a worldwide accepted energy vector whose widespread limitation is mainly associated with its storage in a compact, safe, and cost-effective manner [1]. Formic acid (FA) has recently appeared as a stable and readily available liquid-phase chemical hydrogen storage material, whose high gravimetric and volumetric hydrogen capacities, together with its non-toxicity make it a promising candidate to be used to this end. A screening of carbon-supported PdAg nanoparticles (PdAg/C) were assessed in the decomposition of FA.

Experimental

PdAg NPs with a wide compositional range in terms of PVP/metal and Pd/Ag molar ratios were prepared in colloidal form and subsequently deposited on activated carbon.

Results and discussion

The catalytic activities depended on Pd/Ag and PVP/M ratios. H_2 output increased with the Ag content until reaching an optimum Pd/Ag ratio (Pd/Ag=½). Further incorporation of Ag resulted in a catalytic activity decay. The highest H_2 production (266 μmol) was achieved with the catalyst prepared by using the colloid with PVP/M=1. The characterization of these samples indicated that the best performance achieved by this sample is ascribed to its optimum composition and electronic features.

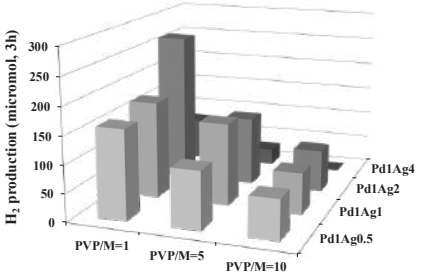

Figure 1. H_2 output after 3 h of reaction at 30 °C for all the studied PdAg/C catalysts.

Conclusions

The evaluation of the catalytic performance combined with the detailed characterization indicated the beneficial effect of the Ag incorporation and revealed that the best performance achieved by Pd1Ag2/C (PVP/metal = 1) can be ascribed to its optimum composition and electronic features.

Acknowledgements

MNG thanks the Japan Society for the Promotion of Science (JSPS, A17F173810 y J171015004) and the Generalitat Valenciana (project Plan GenT, CDEIGENT/2018/027) for the financial support.

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P54

Evaluation of electrocatalytic stability of electrodes prepared by the solvothermal deposition of cobalt sulphides on carbon cloth

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Introduction

Water electrolysis is an attractive way to produce pure hydrogen, but it is limited by the slow kinetics of electrode reactions. To improve the efficiency of the process, the search for cheaper and active electrocatalysts is important. Promising materials are efficient catalysts based on inexpensive non-noble metals. Currently, an attractive approach is to apply the catalyst directly to the surface of the conductive carrier.

Experimental

Here in, we directly deposited the cobalt sulphide nanoparticles on a carbon cloth using a simple one step solvothermal synthesis. The accepted molar ratio Co/S = 1/5 determines the formation of the structure of nanoparticles on the carbon cloth's surface. Prepared composite electrodes were tested for electrocatalytic stability during storage in oxidative conditions. The synthesized electrodes were stored in: air, argon and a mixture of argon and oxygen. To compare the stability of electrodes stored under different conditions, their catalytic activity in hydrogen evolution (HER) and oxygen (OER) reactions were researched at specific intervals of storage. Overpotentials in HER and OER were compared and collated with designated electrochemically active surfaces.

Results and discussion

A freshly prepared composite electrode required overpotentials of 260 mV for HER and 320 mV for OER to ensure a current density of 10 mA cm^{-2}. However, the electrocatalytic activity decreased during stored electrodes in oxidative conditions, especially in HER. The overpotential of hydrogen evolution of electrodes stored in the air, to ensure the current density of 10 mA cm^{-2}, increased by 75 mV in 30 days. For comparison, the overpotential of hydrogen evolution of electrodes stored in argon, to ensure the current density of 10 mA cm^{-2}, increased by 37 mV.

Conclusion

The initial overpotentials in HER and OER prove the high application potential of composite electrodes based on cobalt sulphide in a strongly alkaline electrolyte. The results show that the cobalt sulphide nanostructure, applied directly by the solvothermal method, is not stable in contact with oxygen. Research shows that in order to preserve high activity in HER and OER, it is necessary to store such electrodes in conditions of the smallest oxygen content. Restrictive operational conditions reduce their attractiveness in potential commercial applications.

Acknowledgements

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P55

Electro-oxidative behavior of lignin-derived Pt supported carbon (submicron) fibers and effects on the activity for alcohol electro-oxidation

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Introduction

We recently reported an innovative single-step preparation method of Pt-supported (submicron)carbon fibers, with and without phosphorus, through electrospinning of lignin solutions [1]. Besides good flexibility and high surface area and electrical conductivity, these fibers were found to exhibit outstanding catalytic performance in the electro-oxidation of methanol and ethanol. This work presents a systematic and detailed investigation on the electro-oxidative behavior of these type of fibers, paying special attention on their electrochemical stability, physicochemical changes and effects on their activity for alcohol electro-oxidation.

Experimental

For their preparation, the electrospun fibers were thermostabilized in air and carbonized at 900 ºC. The materials were thoroughly characterized by different techniques (XPS, TPD, TEM, XRD and CV and chronoamperometry in the presence and absence of alcohols, e.g. MeOH, EtOH) before and after various (voltammetric or potentiostatic) electro-oxidative treatments. The influence of phosphorus and the Pt loading (1-5 wt%) was analyzed.

Results and discussion

Changes in CV profiles (Fig. A) clearly indicate that Pt-containing carbon fibers can be electro-oxidized at 1.1 V. Instead, the electrooxidation resistance of the fibers greatly increases in the presence of phosphorus. The obtain results show that pristine Pt-containing fibers, without any pre-treatment, exhibit a poor performance for MeOH electro-oxidation (Fig. B). However, after the electro-oxidative treatment in H_2SO_4, the fibers seem to be activated for MeOH oxidation (Fig. B). Nevertheless, the electroxidation of fibers at too-high potentials can be detrimental for this reaction.

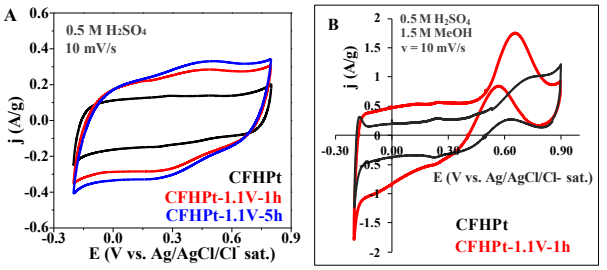

Figure. Cyclic voltammograms of Pt(5wt%)-CFs before (CFHPt) and after oxidation at 1.1 V for 1-5 h in the absence (A) or presence of MeOH.

Conclusions

The electrochemical oxidation of the studied Pt-supported CFs seems to cause an important effect on their activation for alcohol electro-oxidation.

Acknowledgements

MINECO and FEDER funds (RYC-2017-23618, MAT2016-76595-R, CTQ2015-68654R).

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P56

Palladium nanoparticles supported on carbon materials as methanol oxidation catalyst

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Introduction

Energy conversion and generation have generated a great attention in the last decades in order to develop alternative technologies to replace the use of fossil fuels. Direct methanol fuel cells (DMFC) are considered as devices of great interest for obtaining clean energy because of the abundance of the fuel, its easy storage and safety in the use of methanol. However, one important limitation is the electrocatalyst for methanol oxidation due to the low activity, the short durability and the high price. Thus, the development of catalysts for the methanol oxidation reaction (MOR) is of great interest

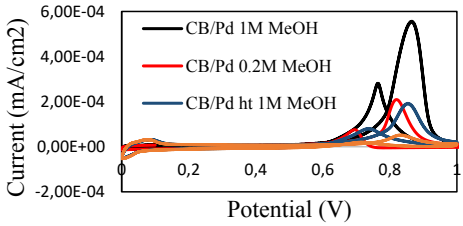
Experimental

In this work, catalysts based on palladium nanoparticles synthesized by the reduction-by-solvent method supported on carbon materials have been used for the oxidation of methanol. The synthesis was carried out dissolving, on the one hand, the required amount of palladium using $Pd(ac)_2$ precursor in dioxane, under stirring at room temperature. On the other hand, the amount of PVP required to get a ratio PVP/Pd=10 was dissolved in ethylene glycol at 80°C and under stirring for 1 h. The Pd nanoparticles were supported on commercial carbon black using the impregnation method.

Results and discussion

The final loading of Pd determined by ICP is 3 wt%. This catalyst was treated at 450ºC in N_2 atmosphere to study the effect of protecting agent in the MOR.

The activity and durability of these catalysts has been studied by cyclic voltammetry. The catalytic properties have also been studied by in-situ FTIR to observe the different reaction products obtained and to get information about the reaction mechanism.



Conclusions

As can be seen in the results obtained, a higher peak current of methanol oxidation is obtained for the catalyst which has not been thermally treated. Therefore, a positive effect of the heteroatoms bound to the Pd species for the MeOH reaction is observed

Acknowledgements

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P57

3D Structure of Pd Based Catalysts Supported on Cellulose-Derived Carbon

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Introduction

This work presents the use of the Electron Tomography (ET) technique to explain activity of the metallic catalysts/cellulose derived carbon on liquid phase reactions [1].

Experimental

The Pd and Pd-Al/CDC catalysts have been prepared by thermal decomposition of impregnated cellulose under reductive atmosphere [1]. The catalytic hydrogenation of cyclohexene (CE) was used as test reaction carried out in a high pressure batch reactor.

Results and discussion

Surprisingly, the TOF results obtained indicate that the more sintered catalyst shows the highest activity, Fig.1a. ET characterization unambiguously demonstrates that the smaller Pd NPs are inactive because leave confined in the internal structure of the support (see Fig. 1b). In contrast, the larger Pd NPs formed at higher preparation temperatures are placed at the external surface of the catalyst, being accessible to the reactants (see Fig. 1c).

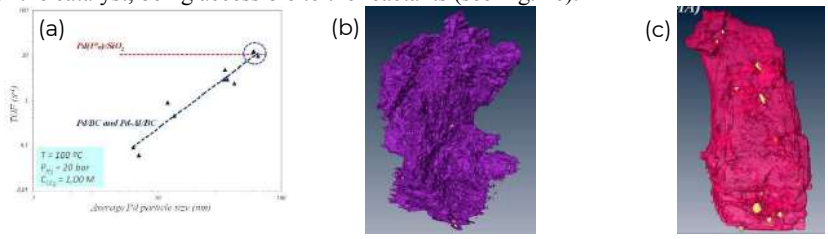

Fig 1. (a) Evolution of the Turn over frequency (TOF) vs. the average particle size. (b) 3D reconstruction of the Pd-Al/CDC catalyst prepared at 600 ºC and (c) 800 ºC.

Conclusions

The application of the ET allows to explain the results obtained in the CE hydrogenation using Pd and Pd-Al/CDC catalysts, allowing the optimization of their synthesis.

Acknowledgements

We acknowledge financial support from MINECO (Spain) Project ENE2017-82451-C3

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P58

Study of cobalt-oxides supported on activated carbon as electrocatalysts in hydrogen evolution reaction

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Introduction

Hydrogen is considered as the most sustainable energy source to substitute the current energy sources based on fossil fuels. Therefore, the development of alternative non-noble metal electrocatalysts based on abundant and low-cost materials has attracted considerable attention [1]. In this work, we propose the development of copper-doped cobalt oxides supported on activated carbon (AC).

Experimental

The electrocatalyst materials were prepared following the procedure described elsewhere [2].

Results and discussion

The electrocatalyst that exhibits the best performance towards HER is the sample that contains 20% of $CuCo_2O_4$ supported on the AC. The good activity of the hybrid material is related to a synergistic effect of both materials.

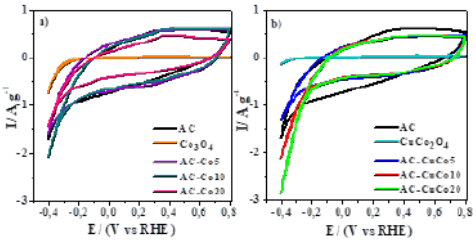

Figure 1. CV recorded in 0.1 M KOH: a) undoped AC-Cox samples and b) copper-

Conclusions

The copper-cobalt spinel supported on AC is a promising alternative to substitute the commercial electrocatalysts towards HER.

Acknowledgements

The authors thank MINECO and FEDER (MAT2016-76595-R and ENE2017-90932-REDT). J.X.F.-L. gratefully acknowledges MINECO for the FPI grant (BES-2017-081598).

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P59

Doped Carbons in Electrocatalytic Processes

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Introduction

Climate change and global warming are issues of concern in today's society. Different techniques have been proposed to reduce the CO_2 emissions, and the electrochemical reduction of CO_2 to obtain biofuels is one of the most suitable ways to reduce the amount of CO_2 emitted to the atmosphere. Typical systems used are metal-based catalysts[1]. In this work, mesoporous N-doped carbons have been prepared as a metal-free alternative, using melamine and calcium citrate as precursors.

Experimental

N-doped carbons have been prepared using melamine and calcium citrate. They have been mixed homogeneously and pyrolyzed at different temperatures under flowing N_2 for 1 h. Also, samples with different ratios of melamine and calcium citrate have been synthesized by pyrolysis at 800ºC for 1 h. Then, calcium oxide is removed by treatment with HCl 1M and, finally, carbons are washed with distilled water and dried. The carbons were characterized by XPS, N_2 adsorption isotherms at -196ºC and Raman spectroscopy.

Results and discussion

The carbons obtained at temperatures higher than 750 ºC present a porous development with an increase in surface area from 258 to 388 $m^2 \cdot g^{-1}$ (Figure 1). Surface composition has been analyzed by XPS. The nitrogen content is very high even at high temperatures, being 15 at.% for materials pyrolyzed at 850ºC.

The effect of the melamine:citrate ratio is evident, and 1:1 is the most suitable ratio to obtain a high surface area and mesoporosity. The amount of nitrogen also depends on the ratio, and the highest nitrogen content is obtained for MelCit (2:1) (18%).

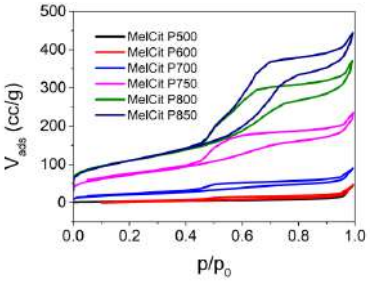

Figure 1: N_2 adsorption isotherms at -196ºC for MelCit serie pyrolyzed at different temperatures.

Conclusions

The synthesis proposed is an easy way to obtain mesoporous N-doped carbons with no further activation treatment. With this method, a high porous development has been achieved and the superficial nitrogen amount is between 15 and 25 at.%.

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P60

SiC-Pt catalysts as an alternative to classic carbon-Pt catalyst for high-temperature processes.

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Introduction

Sintering due to lack of bonding with the support is the main deactivating mechanism operating in carbon-Pt catalysts. This phenomenon becomes more evident in high-temperature processes where the sinterability of the metal particles increases. Silicon carbide (SiC) is an attractive alternative to be used as catalyst support in high-temperature reactions because of its high thermal conductivity, chemical inertness (even under oxidizing conditions), and its ability to hinder sintering of the active phase by chemically bonding the metal to the support through the formation of a silicide interface.

Experimental

In this work, porous SiC, produced through a hard template method (carbothermal reduction of SiO_2), has been impregnated with Pt (1 and 5 wt.%) and used in the catalyzed crotonaldehyde hydrogenation reaction. Activity and selectivity of the catalyst have been measured and correlated to its microstructure and surface chemistry. The catalyst (Pt/SiC) has been characterized at the different stages using TGA, N_2 adsorption, TEM and XPS.

Results and discussion

The activity and selectivity is similar to that obtained with carbon as support. However, when the reduction is carried out at higher temperatures 500-700 C, the activity is maintained, which is the main difference with carbon supports. This is because Pt sintering does not occur.
Through studies of XPS it is observed that Pt particles reacts with SiC forming silicides at the interface, that is why it prevents them from sintering.

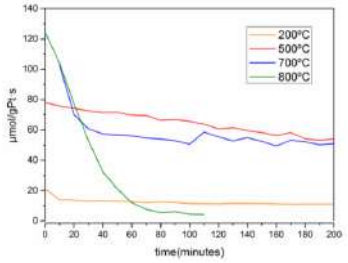

Figure 1. Activity crotonaldehyde hydrogenation reaction at different temperatures of reduction.

Conclusions

SiC-Pt catalysts can be prepared which can work at high activity up to 700ºC compared to other types of carbon supports at high temperatures.
The particles after the reduction have a small size barely sintered because they have reacted with the SiC and fixed them to the support.

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P61

Treatment of real brewery wastewater by aqueous phase reforming with carbon supported Pt catalysts

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Introduction

Aqueous phase reforming (APR) has gained an increasing attention since the pioneering work of Cortright et al. [1], where production of valuable gases, such as H_2, from biomass-derived compounds was reported. A previous work has shown that APR can be used as a wastewater treatment process where simultaneous elimination and valorisation of biomass contaminants is achieved [2]. In this work APR is applied to the treatment of real brewery wastewater (RBW).

Experimental

APR runs for the treatment of RBW (TOC = 1646 mg/L, COD = 4674 mg/L, pH 11) was studied in batch runs at 493 K and 24-28 bar, using different 3% Pt/C catalysts prepared by incipient wetness impregnation on two carbon blacks (ENSACO, Ketjenblack) and an activated carbon (Merck). Gases were collected in multifoil bags and analysed by GC/FID/TCD.

Results and discussion

Treatment of RBW by APR resulted in high TOC and COD removal (57-78 %). Higher TOC and COD removal were observed for catalysts supported on carbon blacks. The gas produced was mainly composed by CO_2, H_2 and CH_4, and virtually free from CO. In blank experiments (no catalyst) around 20 % of TOC and COD was removed and the gas produced was basically CO_2. Catalysts supported in carbon blacks also led to higher organic carbon conversion to gas (*CCgas*) and hydrogen yield Y_{H2}.

Catalyst	Gas composition (% mol)			*CC gas (%)*	Y_{H2} (mmol H_2/gCOD)
	H_2	CO_2	Alkanes		
Blank	0.9 ± 0.6	94.2 ± 2.1	3.6 ± 0.2	3.3 ± 0.1	< 0.1
Pt/ENSACO	51.1 ± 3.2	28.8 ± 2.1	20.1 ± 1.1	27.0 ± 4.0	7.8 ± 1.4
Pt/Ketjenb	53.6 ± 6.3	26.5 ± 5.6	19.9 ± 0.7	40.0 ± 2.9	12.9 ± 2.3
Pt/MerK	11.7 ± 6.9	78.9 ± 7.6	9.4 ± 0.7	8.5 ± 1.0	0.3 ± 0.3

Conclusions

APR enabled successful treatment of RBW and high H_2 and CH_4 production. Customization of the catalyst is needed as high influence of the catalyst support was observed.

Acknowledgements

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P62

Electrochemical Tunable Biosensors Employing Carbon Nanotubes Modified with Phosphorus species for Amperometric Glucose Detection.

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Introduction

Nitrogen functionalities, such as amines; carboxylic groups and phosphorus-containing species on the carbon materials have shown a remarkable performance in the immobilization of different biological bioreceptors, by both covalent and electrostatic interactions with the bioreceptor elements. At the same time, these functionalities on the carbon material electrode have demonstrated to promote the electron-transfer and modulate the sensitivity and detection range of the analyte of interest.

Experimental

MWCNTs electrode have been modified electrochemically with 4-APPA following a previously published procedure [1]. Subsequently, GDH-s-PQQ is immobilized onto the electrode synthesized and tested by chronoamperometry, towards glucose oxidation.

Results and discussion

MWCNTs modified with 4-APPA at different potentials present electrocatalytic activity towards glucose oxidation. Depending on the potential used in the electrochemical modification, different detection range, sensitivity and enzyme-substrate interaction are observed.

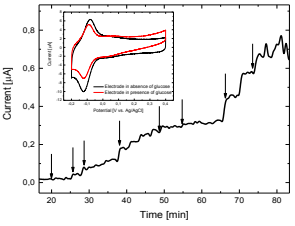

Fig. 1. Chronoamperometry at 0.35 V of MWCNT electrochemical modified with 4-APPA at 1.4 V after continues glucose addition

Conclusions

Operational sensing parameters and electrochemical performance of the MWCNT modified with 4-APPA and GDH-s-PQQ can be modulated by the potential of modification, obtaining high sensitivity or wide detection range towards glucose oxidation, proving to be a good platform for biosensing.

Acknowledgements

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P63

Catalysts for biomass transformation into added-value products

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Introduction

The shortage of fossil fuels and the environmental pollution caused by their use has led to strongly promote renewable sources to obtain chemical products by clean and eco-friendly methods. In this context, exploitation of lignocellulosic biomass implies the use of renewable resources and the revaluation of wastes, such as those from agriculture or forestry industries. Acid hydrolysis of lignocellulosic biomass yields levulinic acid (LA), which can be further transformed into high added-value compounds [1]. The present study focuses of the development of catalysts based on Ru supported on TiO_2 or activated carbon (AC) for conversion of LA into γ-valerolactone (GVL).

Experimental

Titania P25 from Degussa, TiO_2 synthesized by sol-gel method (named TiO_2-SG) [2], a commercial AC from MeadWesvaco (named SA), and an AC synthesized by hydrothermal carbonization of almond shells (named CCA) were used as supports. They were impregnated with $RuCl_3$ aqueous solution to obtain 1 and 5 wt. % Ru (nominal). The catalysts were characterized by XPS, TEM and DRX. Conditions of the catalytic tests were: 0.445 mL LA, 130 mg catalyst and 25 mL distilled water, 170ºC, 20 bar H_2, 3 h reaction time (but 1.5 h in one particular experiment), under stirring. The liquid reaction products were analysed by HPLC.

Results and discussion

Fig. 1 shows that a high LA conversion has been achieved with all the catalysts. Regarding selectivity, the obtained data shown that it is higher when the Ru loading is 1 wt %. The nature of the support used is, however, less significant. When the catalytic test is performed only for 1.5 h (with P25-1Ru catalyst), conversion and selectivity are very high, meaning that the reaction time should be shortened to avoid any conversion or further degradation of the target product (GVL).

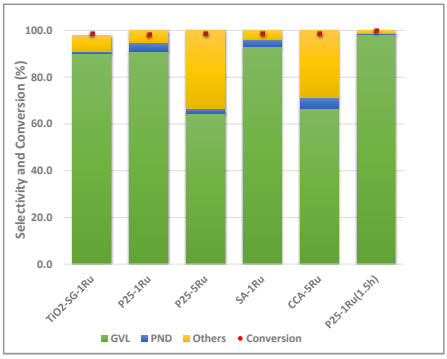

Figure 4. *LA conversion (red points) and selectivity to different products (bars).*

Acknowledgements

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P64

Solar photodegradation of acetaminophen with TiO_2/activated carbon heterostructures: the effect of the activating agent.

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Introduction

The treatment of water effluents with contaminants of emerging concern, such as pharmaceuticals and personal care products (PPCPs), is receiving special attention because of their negative impacts for both human health and the environment [1-2]. In this context, there is a growing demand for technologies that can deal with these emerging contaminants in cost-effective terms. The combination of TiO_2 with carbonaceous materials can result in active heterostructures for the photocatalytic removal of PPCPs under solar light.

Experimental

Several activated carbons (ACs) were prepared by chemical activation of lignin with different activating agents ($FeCl_3$, $ZnCl_2$, H_3PO_4 and KOH) and used for synthesizing TiO_2/activated carbon heterostructures via solvothermal treatment. The synthesized materials were fully characterized and further used in the photodegradation of a target pharmaceutical compound (acetaminophen, ACE) under solar simulated irradiation. Settling experiments and stability of the photocatalysts were also investigated.

Results and discussion

The porous texture and surface chemistry depended on the chemical compound used to activate the lignin. XRD patterns confirmed the presence of anatase phase, regardless of the activated carbon used, with crystal sizes close to 10 nm in all cases, without the need of an additional heat-treatment step. Among all heterostructures, the obtained by $FeCl_3$-activation yielded complete conversion of acetaminophen after 6 h of reaction under solar-simulated irradiation. Although the reaction rate was lower than that observed with bare TiO_2, the heterostructure showed significantly higher settling velocity, thus being considerably easier to recover from the reaction medium. It also showed a good performance in the photocatalytic oxidation of ACE after four successive cycles.

Conclusions

Solvothermal synthesis of TiO_2/AC heterostructures was successfully achieved. ACs showed a well-developed porous texture and different surface functional oxygenated groups and acid-basic character depending of the activating agent used. TiO_2/Fe-C showed the best conversion rate in the degradation of ACE under solar light. Settling experiments demonstrated the easier recovery of the heterostructured material than bare TiO_2. TiO_2/Fe-C also showed a good performance in the photocatalytic oxidation of ACE after four successive cycles, maintaining its initial activity.

Acknowledgements

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P65

Carbon xerogels for the removal and photodegradation of Yellow-5 under solar irradiation

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Introduction

Environmental pollution and the production of clean energy are two major goals for the XXI century. Photocatalysis has emerged as a sustainable process for water remediation using active carbons with high microporosity [1]. However, in water treatment processes the so called feeder pores play an important role. Synthetic carbons with very well controlled porous structure were produced with analogous surface chemistry and microporosity, being the feeder pore size the only difference. The role of the mean pore size on the adsorption capacity and photodegradation of yellow-5 (Y-5) was evaluated.

Experimental

Organic xerogels were synthesized from polymerization of resorcinol (R) and formaldehyde (F) mixtures in water under microwave heating. Porous structure can be design by tuning the synthesis variables [2]. A series of organic xerogels with different pore size (i.e. 5, 10, 20, 40 and 100 nm) were obtained. The polymers were carbonized under nitrogen flow at 1000ºC and denoted as CX (for Carbon Xerogel). The kinetics of adsorption and photodegradation under solar irradiation of yellow-5 (Y-5) were performed. Results were compared as a function of the surface density of molecules and the textural properties of the carbon xerogels.

Results and discussion

An optimum feeder pore size for Y-5 adsorption in the dark (i.e. 20 nm) was found. The narrow mesopores (i.e. 5 nm) inhibit the diffusion of Y-5; while the samples with wider pores (i.e. 40 and 100 nm), showed a low uptake. Contrary to nanoporous carbons [1], CX exhibit very low photocatalytic activity, but a synergistic effect was found TiO_2-P25, improving the disappearance of Y-5. This synergy effect is highly dependent of the initial concentration of Y-5 suggesting mass diffusion from bulk of solution is the driven force for the adsorption and the photocatalytic activity.

Conclusions

The mean pore diameter of CX influences the uptake of Y-5, and the maxima photocatalytic activity was found for pores of ca. 20 nm. The photoactivity was highly affected by the initial concentration of Y-5 suggesting that intraparticle diffusion model play an important role on the diffusion of Y-5 molecules from the bulk of solution.

Acknowledgements

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P66

Photovoltaic efficiency of solar cell based on fluorinated carbon nanotubes/n-doped Si

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Introduction

One of the most promising photovoltaic device is considered to be one based on single-walled carbon nanotubes (SWNTs) deposited on n-doped Si. Single-wall semiconductor nanotubes are preferred for use as a component in photovoltaic devices. SWNTs effectively absorb light in the near infrared range, which allows to expand the optical absorption spectrum of device. The increase in photoelectric conversion efficiency is also associated with the high mobility of electrons and holes in SWNTs. Fluoridation of SWNTs should convert metallic SWNTs to semiconducting what improves photovoltaic response with a linear dependence of the current density from the voltage.

Experimental

Fluorination of SWCNTs was performed in BrF_3/Br_2 solution. Process of fluoridation was carried out for 7 days in a tightly closed teflon reactor at room temperature. After that time, the samples were purged with N_2 to remove remaining reaction mixture. Fluorinated single-walled carbon nanotubes (F-SWNTs) were sonicated in dichlorobenzene to form stable suspensions. The resulting suspensions were filtered through the nitrocellulose membrane. As a result, F-SWNT films with a thickness of ~200-300 nm covered the membrane surface were obtained. Then film of F-SWNTs was transferred to silicon substrate. As a result, the F-DWNT films were covered about 20% of 1 cm^2 n-Si surface. Indium tin oxide glass was placed on silicon substrate with F-SWNTs to perform the photovoltaic experiments. The measurements were carried out with change of resistance from 0.1 kOhm to 4700 kOhm at different light flux.

Results and discussion

In the present work applicability of fluorinated SWNTs to improve the efficiency and stability of photovoltaic cells was tested.

Conclusions

An improvement of photovoltaic response after fluorination of SWNTs was demonstrated. Measurements of electrical conductivity showed that the resistance of the F-SWNT films depends on degree of fluorination.

Acknowledgements

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P67

Synthesis and characterization of reduced oxide graphene/TiO_2 composites for the degradation of ethylparaben under UV irradiation

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Introduction- Parabens, a group of alkyl esters of p-hydroxybenzoic acid, are widely used as preservative and antimicrobial agents in food and cosmetics, and are currently considered as potential emerging contaminants in the environment [2]. To guarantee the minimum discharge of this pollutant in the future the implementation of new technologies is necessary. In particular, graphene nanomaterials in combination with TiO_2 highlight new prospectives in the field of photocatalysis. The aim of this study was to determine the effectiveness of GO/TiO_2 composites in the degradation of ethylparaben (EtP) under UV irradiation. For this purpose, we synthetized and characterized GO/TiO_2 composites with different graphene oxide (GO).

Experimental- GO/TiO_2 composites were synthetized by a hydrothermal treatment, employing titanium isopropoxide and graphene oxide (GO) as starting materials [2]. The composites were characterized by DRS, HRTEM, Raman spectroscopy, FTIR, XPS and XRD in order to analyze the structure and morphology of the samples. EtP degradation experiments were conducted in an ultraviolet laboratory reactor system 2, equipped with a medium-pressure mercury vapour lamp. EtP concentrations in solution were determined by HPLC

Results and discussion- The characterization of the composites using different techniques confirmed the successful reduction of the graphene oxide and the polydisperse presence of TiO_2 into the structure. The synthetized GO/TiO_2 composites exhibited superior photocatalytic activity in the degradation of EtP compared with TiO_2. The intimate contact between TiO_2 and GO leads to an increase in the transfer of photogenerated electrons on TiO_2 to GO, leading to an effective charge anti-recombination and thus enhancing the photocatalytic activity.

Conclusions- The obtained results confirmed the potential of GO to blend with TiO_2 and to produce effective composites for the photocatalytic treatment of wastewaters, in particular those polluted with parabens.

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P68

Solar degradation of the sulfamethazine drug assisted by rGO/Bi photocatalyst

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1. Introduction – Sulphametazine (SMZ) is an anti-infective agent widely used due to its strong antimicrobial activity. Recent studies demonstrated that prolonged exposure to low concentrations of antibiotics accumulated in water can be health hazard. To guarantee the minimum discharge of this pollutant in the future the implementation of new technologies is necessary. The formation of transition metal oxides on the surface of graphene has been shown to be highly efficient in AOPs [1]. The aim of this study was the synthesis and characterization of a novel bismuth composite supported on graphene sheets (rGO/Bi). The degradation of sulfamethazine (SMN) by solar radiation in the presence of this composite material was evaluated.

2. Experimental – Graphene oxide (GO) was synthesized using a modified Hummer's method [2]. rGO/Bi composites were obtained from GO using heat treatment in a microwave with 1500W power. Different rGO/Bi proportions, temperatures and times were tested to reach the optimum composite.

The structure, morphology/microstructures and functional groups have been investigated through different characterization techniques: diffuse reflectance (DRS), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), RAMAN spectroscopy, Fourier transform infrared spectroscopy (FTIR) and X-Ray diffraction (XRD). Photocatalytic tests of SMZ were conducted by a solar box reactor equipped with a Xenon lamp of 1500W.

3. Results and Discussion - The characterization of this material using different techniques confirmed the successful reduction of the graphene oxide and the polydisperse presence of Bi into the structure. The photocatalytic performance test of the synthesized rGO/Bi composite showed excellent photocatalytic activity, degrading 100% of SMN after 120 min under solar light irradiation. The adsorption experiment verifies that the composite material does not act as an adsorbent but as a catalyst of the photochemical reactions involved. Moreover, the obtained catalysts are reusable up to a minimum of 3 cycles without losing their properties. The cytotoxicity assay confirmed the non-toxicity of the degradation byproducts, indicating the potential application of this material in real treatment plants for the selective removal of antibiotics.

4. Conclusions - The results obtained showed the great effectiveness of rGO/Bi composite as photocatalyst to remove sulfamethazine from water.

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P69

TiO_2/carbon materials for photocatalytic generation of H_2 from methanol

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Introduction

The development of more efficient TiO_2 materials for applications in photocatalysis, especially those aimed to environmental and energetic issues, is a subject of interest. As TiO_2/carbon composites are considered a promising alternative [1], this work focuses on a hybrid material prepared with carbon black (CB) and commercial titanium dioxide P25. This composite material was tested in the photocatalytic generation of H_2 from methanol [1]. Note that, from an application point of view, methanol can be produced by the photocatalytic reduction of CO_2.

Experimental

0.1 g CB and 0.5 g TiO_2-P25 were added simultaneously (one-pot) to 150 mL HNO_3 10 M. The suspension was heated up to 110ºC and stirred for 3 h in a round bottom flask with a condenser. After cooling down, the suspension was washed with distilled water, until neutrality. Then, the recovered solid was dried overnight at 110ºC and labeled as $(CB\text{-}TiO_2)_{ox}$. This composite material, and also the two individual components, TiO_2-P25 and CB, were characterized (N_2 adsorption, XRD) and tested in the photocatalytic generation of H_2 from methanol in liquid phase using 350 mL of 2.5 M methanol solution, 0.17 g catalyst, 20 ml/min He flow for 2 h, and a 365 nm Hg lamp (TQ-150, 146 W/m^2), being the products quantified by mass spectrometry.

Results and discussion

The composite photocatalyst has slightly higher surface area than TiO_2-P25 (69 vs 58 m^2/g) and, as expected, these two samples have similar crystalline compositions and sizes. The TEM images show that the particle size of the composite material is slightly lower than that of TiO_2-P25, probably due to the experimental preparation procedure. The composite material showed the highest photocatalytic efficiency for H_2 generation from methanol (4.08 μmol in 2 h), nearly 9 times greater than the efficiency of TiO_2-P25 (0.47 μmol in 2 h). CB was not active for H_2 generation and photolysis was discarded.

Conclusions

$(CB\text{-}TiO_2)_{ox}$ has shown a significant enhancement of the photocatalytic generation of H_2 from methanol respect to TiO_2-P25, showing that TiO_2/carbon materials are interesting for this application. Further research is required to determine the role of the CB incorporation and of the oxidation treatment.

Acknowledgements

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P70

TiO_2-carbon hybrid photocatalysts for the elimination of pollutants in liquid phase

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Introduction

Among the different available strategies to improve the TiO_2 photocatalytic efficiency, its combination with carbon seems to be effective [1]. The present work focuses on the preparation of TiO_2-AC (activated carbon) samples and their application to liquid phase processes with environmental and energetic interest: 1) acetic acid (HAc) decomposition to produce biogas and hydrogen and 2) degradation of the pesticide diuron.

Experimental

TiO_2-AC photocatalysts were prepared by adding a certain amount of a spherical AC during the sol-gel TiO_2 synthesis in order to have 0.5, 1 and 10 wt.% C. The AC was previously obtained by hydrothermal treatment of saccharose. The photocatalysts, named TiO_2-AC**x** (**x** = C wt.%), were characterized by N_2 adsorption-desorption at -196 ºC, XRD, TG analysis and SEM. The reaction conditions of the two processes mentioned above were: i) HAc decomposition: 350 mL of 1 M HAc, 0.35 g catalyst, 12 h, 365 nm Hg lamp (TQ-150, 146 W/m^2), being the products (CH_4 and CO_2) quantified by mass spectrometry; ii) diuron degradation: 100 mL of 10 mg/L diuron solution, 0.1 g catalyst, in a solar chamber (ATLAS, Suntest XLS+, 340 nm lamp, 250 W/m^2); UV-vis spectroscopy was used to determine the diuron concentration. P25 commercial titania was used for comparison purpose.

Results and discussion

The carbon content values of the TiO_2-AC samples are slightly lower than the nominal ones. They contain only anatase, in a proportion lager than P25 and with lower crystal size, and they have larger surface area.

In HAc oxidation, the prepared samples are, in general, more active than P25, producing more CH_4 and leading to a higher CH_4/CO_2 ratio. In general, the presence of AC seems to improve the catalysts efficiency respect to that of TiO_2 synthesized without AC. Among the TiO_2-AC catalysts, TiO_2-AC**1** displays the highest activity. Likely, a higher AC loading might hinder the light interaction with the TiO_2 surface.

The removal of diuron is the highest in TiO_2-AC**10** followed by P25. The good behaviour of this catalyst is likely related with a combination of two processes: diuron adsorption on the AC and its photooxidation.

Conclusions

The presence of carbon during the synthesis of TiO_2 photocatalysts leads to interesting materials for the two studied reactions. TiO_2-AC**1** shows the best results in HAc oxidation, whereas TiO_2-AC**10** shows to be better for diuron removal. The positive effect of carbon could be attributed to an increase of the catalysts surface area, to the decrease in the recombination rate of electron-hole pairs and also, in some cases, to favored adsorption processes.

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P71

TiO_2-based materials for the photocatalytic oxidation of propane. Study by *in-situ* DRIFTS

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Introduction

As propane is widely used as fuel, and thus is a common component of exhaust emissions, its removal constitutes an important environmental concern. It is a very stable compound because of the difficult activation of its C-H bonds [1] and, among the techniques available for propane removal from gas emissions, photocatalytic oxidation with TiO_2 materials is a promising one. This work deals with the preparation and characterization of TiO_2-based materials and their application to the gas phase propane oxidation.

Experimental

TTIP (4 ml) and ethanol (20 ml) were magnetically stirred (1 h) and treated in ultrasounds bath (30 min). Then, a solution containing HCl of variable concentration (0.5-12 M, 4 ml) and ethanol (10 ml) was added dropwise, followed by 1 h stirring. Afterwards, the mixture was submitted to a hydrothermal treatment (180 °C, 12 h in a 50 ml Teflon-lined stainless-steel autoclave). The resulting solid was filtered, dried (100 °C, 12 h) and heat treated (air, 5 °C/min, 350 °C, 2 h). The TiO_2-C materials were prepared in the same way, but adding 1.25 g saccharose to the TTIP/EtOH mixture. The photocatalysts were characterized (N_2 adsorption, XRD and UV-vis) and their activity for propane oxidation was studied in a batch reactor connected to a gas chromatograph. Propane adsorption was evaluated in dark conditions (10 min) and illumination (UV-LED of 365 nm and 135 mW) was then switched on for 10, 20, 30 and 60 min intervals. *In-situ* DRIFTS analysis was used to determine reaction intermediates.

Results and discussion

Propane adsorption occurs under dark conditions in TiO_2 and TiO_2-C samples. It has been found that in bare TiO_2 samples, the higher the anatase content, the higher the amount of propane adsorbed in dark, whereas rutile and brookite seem to hinder propane adsorption. For TiO_2-C samples (that only contain anatase) a relationship between adsorbed propane in dark and BET surface area has been found. Propane photooxidation is lower with the TiO_2 and TiO_2-C catalysts than with commercial P25, and an almost inverse linear relationship between propane conversion and the amount of propane adsorbed in dark was observed. DRIFTS analysis reveals oxidation intermediates like acetone (ac), formate (form) and bicarbonate species on the photocatalysts surface during reaction. An almost reverse relationship between the form/ac and bic/ac peak heights ratios and the catalytic activity has been observed.

Conclusions

TiO_2 samples are more active for propane oxidation than TiO_2-C ones, and both series are less active than P25. Propane oxidation is inversely related to propane adsorption in dark conditions, which in TiO_2 samples depends on the crystalline phases' distribution, and in the case of TiO_2-C samples depends on the BET surface area.

Acknowledgements

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P72

Photocatalytic degradation of tartrazine using C-doped Cu-/Mo-based catalysts under solar irradiation

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Introduction

Considering the high potential of Cu- and Mo-based materials in optoelectronic applications [1,2], the objective of this study was to obtain C-doped Cu- and Mo-based catalysts for the degradation of tartrazine (*aka* yellow 5) -a dye commonly found in food derivatives- and then to optimize the catalyst load necessary for the total conversion of the dye. To attain this goal, a series of photocatalytic tests were performed with increasing catalysts loadings.

Experimental

The catalysts were prepared using a solvothermal method, and were calcined and pyrolyzed before its use. A kinetic adsorption study of the dye (Y5) was initially carried out in dark conditions until equilibrium was reached. Afterwards, the suspension was exposed to irradiation for 6 hours. The photocatalytic tests were carried out using an initial dye concentration of 5 ppm, and catalysts loading of 0.25, 0.5, 0.75 and 1 g/L.

Results, Discussion and Conclusions

The Cu-based catalysts showed up to 40% conversion of Y5, even for the low loadings; in contrast, the Mo-based ones displayed lower activity (ca. 10-20%) and presented an important lixiviation. The bimetallic Cu-Mo photocatalyst showed similar activity to that observed on Cu-based catalysts, but also suffered the lixiviation issues observed for the Mo-derived ones. The pyrolysis treatment enhanced the photocatalytic activity of the Cu-based materials, compared to calcination. The pyrolyzed Cu-based sample was the most active catalyst. For this material, total photodegradation of the dye was obtained after 5 hours irradiation for a loading of 1 g/L, and with an apparent constant rate of $7.3x10^{-3}$ min^{-1}. For the lowest loading, the apparent constant rate was $2.5x10^{-3}$ min^{-1}. Summarizing, it can be concluded that carbon-doped copper-based photocatalysts displayed good activity under solar irradiation for the degradation of yellow 5, whereas those based on molybdenum showed lower photocatalytic activity and a high lixiviation under our experimental conditions.

Acknowledgements

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P73

Effect of carbon nanofibers on clay/PEDOT nanocomposites for the (electro)adsorption of pollutants

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Introduction

Water scarcity threatening demands the development of efficient and economic technologies for wastewater treatment. Among various possibilities, adsorption has been proved to be a simple and effective technology to remove pollutants from aqueous systems. Nevertheless, its feasible application depends on the cost of the adsorbent. Clay minerals are abundant and inexpensive materials with interesting properties for adsorption. Moreover, their properties can be optimized by modification or combination with other materials, additives etc. This work analyzes the effect of the addition of carbon nanofibers (CNFs) in the performance of a clay and clay/PEDOT hybrids for the (electro)adsorption of diclofenac, an effective anti-inflammatory drug released into the stool and urine [1].

Experimental

A Na-modified montmorillonite (clay), and a clay: PEDOT 1:1 composite and/or with different proportions of CNFs (0-20wt%) were prepared by chemical polymerization of EDOT in the presence of stoichiometric $(NH_4)_2S_2O_8$ oxidant, the clay and/or CNFs. The materials were characterized by gas adsorption, XRD, TG, SEM, XPS, conductivity measurements, cyclic voltammetry and tested for the adsorption and electroadsorption of diclofenac (UV absorption).

Results and discussion

SEM, TG and XPS prove the success of the synthesys method to produce the desired nanocomposite materials. Despite exhibiting the highest microporosity (Fig. A), the clay is able to remove only a 7 % of diclofenac (Fig. (B)). After polymerization, the decrease in N_2 adsorption points out the polymer partly blocks and reduces the clay surface area (Fig. (A)). However, the polymer greatly increases the diclofenac uptake to 93 % (Fig. (B)). CNFs incorporation slightly increases the specific surface area of the nano-composite (Fig. (A)) and its efficiency for diclofenac removal (Fig. (B)), as well as, the electrical conductivity for electrochemical applications.

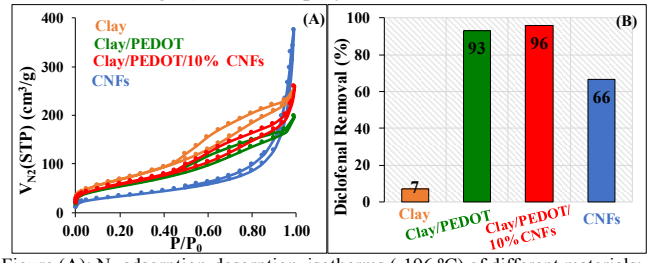

Figure (A): N_2 adsorption-desorption isotherms (-196 ºC) of different materials; and their (B) efficiency for treating a 100 ppm diclof. soltion (25 ºC) after 24 h.

Conclusions

Hybrid clay/PEDOT materials and/or with CNFs show interesting properties for the (electro)adsorption of emerging pollutants present in the water.

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P74

Elaboration of carbonaceous porous materials for the removal of formaldehyde from indoor air by adsorption

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Introduction

Formaldehyde is one of the main indoor air pollutants, because of its ubiquitous presence and its numerous sources of emissions (furniture, flooring and walls…). Its low affinity with several adsorbents and the competition with water vapor limit its removal by adsorption [1]. The physisorption of traces of formaldehyde on Activated Carbon (AC) is favored in micropores [1] and by the presence of nitrogen groups through Van der Waals interactions [2]. Then, our work was focused on the preparation of AC beads with high nitrogen content.

Experimental

A solution of chitosan (average molecular weight: 175 kDa, degree of deacetylation: 89%) at 3.5 wt. % was prepared in formic acid (0.5 mol.L^{-1}) with or without addition of $CuCl_2$ at 5 wt. % relatively to the mass of dissolved chitosan. The solution was added dropwise into a KOH (or NH_3) bath to form hydrogel beads after two hours. KOH (or NH_3) impregnation ratios (IR=$m_{activating\ agent}$ / $m_{chitosan}$) were varied from 20.5 to 135% by changing the concentration of the gelation solution from 2.5 to 15%. The formed hydrogel's beads were filtered and thermally activated at 700 °C (or 900°C) for one hour under a continuous N_2 flow in order to obtain bead-shaped AC. $CuCl_2$ was added to the chitosan solution in order to form metal nanoparticles supported on AC, expected to have a catalytic effect on formaldehyde adsorption.

Results and discussion

The ACs have been characterized by infrared spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), N_2 adsorption-desorption at 77 K and CO_2 adsorption at 273 K. The BET surface area and the mechanical strength of the prepared materials depend on the impregnation ratio (IR). Whatever the KOH IR, the addition of $CuCl_2$ together with the chitosan has yielded to an increase in the mesoporous volume. The KOH IR dependence of the porous volume shows a maximum at 63%, at which microporous-mesoporous AC beads (2 mm diameter) with the highest BET surface area (1000 $m^2.g^{-1}$) and microporous volume (0.4 $cm^3.g^{-1}$) were obtained (with $CuCl_2$ addition). The SEM images of these beads showed multi-scale porosities. X-ray micro-analysis coupled to SEM has brought out the presence of carbon, oxygen, nitrogen and copper. The presence of copper oxides nanoparticles has been evidenced XRD analysis.

Conclusions

N rich activated carbon beads have been synthetized. The adsorption capacities of formaldehyde and water on the activated carbon beads will be determined in future.

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P75

A new method to synthetise activated carbon beads from chitosan for adsorption of formaldehyde from indoor air

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Introduction

Formaldehyde is classified carcinogenic since 2004 [1], is one of the main pollutants of indoor air, because of its ubiquitous presence linked to the numerous sources of emissions (furniture, flooring and walls…). It's difficult to remove by adsorption because of its low affinity with the majority of commercial adsorbents and the competitiveness with water vapor [2]. The physisorption of formaldehyde at low concentration is favored by the presence of micropores and presence nitrogen groups by van der walls interactions [3,4]. In order to effectively treat this compound by adsorption, our research focused on the elaboration of activated carbon beads, if possible with a high nitrogen content:

Experimental

A solution of chitosan (average molecular weight 175 kDa and degree of desacetylation of 89%) at 3.5% wt is prepared in formic acid (0.5 mol. L^{-1}). The solution is added dropwise into a KOH bath to form hydrogel beads. The gelation time is two hours; the beads are then filtered. Different mass impregnation ratios of (wt KOH / Chitosan) were tested by varying the concentration of the KOH bath from 2.5 to 15%. The hydrogels are thermally activated at 700 ° C for one hour (ramp 5 ° $C.min^{-1}$) under nitrogen in order to obtain an activated carbon preserving the shape of bead. Hydrogels have also been prepared by adding to the acid solution of chitosan a metal salt at 5%wt relative to the introduced chitosan, the purpose being to increase the mechanical strength of the activated carbon obtained.

Results and discussion

The activated carbons were characterized by infrared spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), adsorption-desorption of N_2 at 77 K and CO_2 at 273 K. The impregnation ratio in KOH influences the BET surface area and the mechanical strength of the prepared materials. Carbon beads, 2 mm in diameter, are essentially microporous (∅ pores <2 nm) with a ultra microporosity (∅ < 0,8 nm) having a microporous volume of 0.4 $cm^3.g^{-1}$ and a BET surface area of about 1000 $m^2.g^{-1}$ are obtained for an impregnation ratio (mKOH / mChitosan) of 63%. The SEM images of these beads show a macroporosity at several scales. Elemental analysis EDX indicates the presence of carbon, oxygen, nitrogen and copper nanoparticles within the carbon. XRD confirms the presence of copper oxides.

Conclusions

We have synthetized N rich activated carbon beads with a simple method. XPS analyzes will be performed to determine the amount and the types of nitrogen group present in the carbon. Absorption capacities of the material with formaldehyde and water vapor will be tested.

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P76

Predicting the breakthrough profiles of small-scale adsorption columns with emergent pollutants

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Introduction

The increasing presence of emergent pollutants in wastewaters constitutes a growing environmental problem. Adsorption in activated carbons is a suitable process for their removal, and the effect of surface chemistry and porosity on their adsorption kinetics and capacity is well stablished. However, most adsorption studies are performed in batch conditions, while pollutant removal at large scale is done in filter beds. We have reported the prediction of breakthrough profiles of paracetamol in lab-scale adsorption columns of activated carbons using the thermodynamic and kinetic data gathered from batch experiments [1]. In this contribution, we have extended the previous work for predicting the simultaneous breakthrough profiles of two emerging pollutants, what is achieved from independent batch adsorption experiments.

Experimental

H_3PO_4-Activated carbon has been prepared, characterized and used as adsorbent of paracetamol (PA) and carbamazepine (CBZ) solution. The adsorption isotherm and mass transfer constant for the individual pollutants have been determined at low concentrations (similar to those observed at the inlet of sewage water treatment plants) by batch adsorption experiments. Breakthrough profiles for mixtures of these pollutants at the outlet of small-scale adsorption columns have been experimentally determined and compared with predictions obtained from the proposed model and batch data.

Results and discussion

PA and CBZ's adsorption isotherm and heterogeneous effective diffusivity coefficients [1] have been determined by single adsorption using batch experiments. It has been found that bicomponent adsorption can be described using the extended Langmuir isotherm. A kinetic model describing the dynamic adsorption of mixtures of both pollutants in water has been developed. The adsorption data from batch experiments can be feed to the kinetic model, allowing to predict the breakthrough profiles at the outlet stream of small-scale adsorption columns where both PA and CBZ are found in the inlet stream. Figure 1 shows the good agreement observed between the experimental profile and the predictions obtained from the kinetic model.

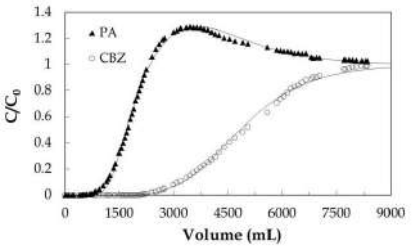

Figure 1. Experimental (dots) and modelled (lines) breakthrough profiles of CBZ and PA.

Conclusions

Bicomponent breakthrough profiles on small-scale adsorption columns can be predicted using adsorption isotherms and kinetic constants from batch single adsorption experiments.

Acknowledgements

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P77

The Effect of Oxidation on the Performance of Carbon Bed Particles in Microbial Electrochemical Fluidized Bed Reactors

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Introduction

We recently reported a new concept in bacteria-electrode interaction based on the use of fluidized carbon-bed electrodes and individual electroactive planktonic living cells [1]. This new concept gave rise to the practical application of Microbial Electrochemical Fluidized Bed Reactors (ME-FBR), e.g. in wastewater treatment. In this work we study the influence of carbon surface chemistry in the interaction and electron transfer with Geobacter cells, and the hydrodynamics and overall performance of the ME-FBR.

Experimental

Two different commercial materials, glassy and activated carbon, were oxidized with boiling 65% HNO_3 for different times or saturated $(NH_4)_2S_2O_8$ in 1 M H_2SO_4 for 24 h. The original and oxidized materials were characterized by XPS, TPD, gas adsorption, Raman; and tested as fluidized bed electrodes (Fig. A), anodically polarized at 0.4 V (vs. Ag/AgCl/Cl-(sat.)), in an anoxic culture medium of electroactive Geobacter Sulfurreducens growing on acetate as sole electron donor and carbon source. Electrical current production and acetate biodegradation rate were monitored with time to calculate the coulombimetric efficiency. The materials were also analyzed by cyclic voltammetry and SEM before and after the studied electrogenic treatments.

Results and discussion

Results show that the functionalization of the carbon materials improves the interaction carbon-bacteria, thus exhibiting a better e-transfer (see the enhanced voltammetric response in Fig B) and the current produced in chronoamperometric experiments. In addition, SEM characterization confirms the promoted interaction.

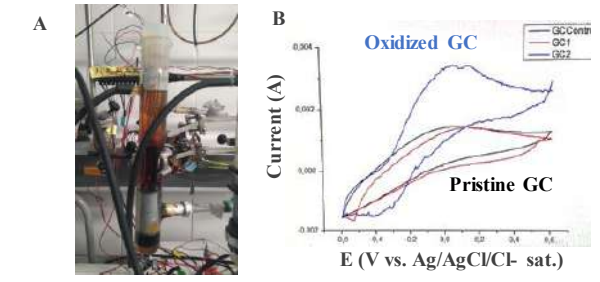

Figure. (A) Experimental set-up and (B) Cyclic volatammograms of of the different materials after innoculation.

Conclusions

The functionalization of carbon materials seems to be a promising strategy to improve the performance of Microbial Electrochemical Fluidized Bed Reactors (ME-FBR).

Acknowledgements

MINECO and FEDER funds (RYC-2017-23618).

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P78

VOCs Adsorption on Doped Carbons

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Introduction

Volatile organic compounds (VOCs) have attracted attention due to the different problems that cause to the human health and to the environment[1]. Adsorption is among the most promising techniques for the removal of VOCs. Activated carbons have been used as adsorbents and it has been demonstrated that their surface modification by doping with heteroatoms such as N could enhance the adsorption capacity for different VOCs[2].

Experimental

Polyaniline (PANI) have been synthesized by two different routes at different temperatures and times (25ºC, 6h and 0ºC, 2h). The polymers were pyrolyzed to obtain the carbons and different steam activation treatments were applied to increase the surface area and create porosity. The samples were analyzed by N_2 adsorption isotherms at -196ºC, XPS, water adsorption isotherms and the adsorption isotherms of different VOCs

Results and discussion

The XPS results show the presence of four nitrogen species on the carbon surface and the N at.% is between 3-7%. Micro-meso porous carbons are obtained with the different activation treatments. Surface area and pore volume increase as the activation temperature and activation time increase, whereas the nitrogen amount decreases. With water isotherms (Figure 1) it is evidenced that the adsorption of water at low pressures is due to the presence of defects (N atoms), while the adsorption at high pressures depends on the porosity of the material. For the case of the toluene adsorption isotherms, the adsorption depends mainly on the porosity of the material.

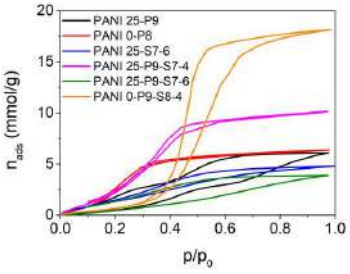

Figure 1: Water isotherms at 25ºC

Conclusions

The obtained carbons present a high surface area and developed porosity after the activation treatments, together with a high N content. The adsorption of water depends on the porosity and nitrogen content, whereas the adsorption of toluene depends mainly on the porosity.

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P79

Degradation of acetaminophen pharmaceutical in aqueous solutions by electro-Fenton process

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Introduction

One of the ecofriendly and more cost-effective version of Fenton-based method, is the electro-Fenton (EF) process. This technology is based on the electrochemical generation of $HO^{\bullet}$ radicals through the *in situ* and continuous electrogeneration of H_2O_2 at a cathode by oxygen reduction reaction (ORR). In this work, metal-free reduced graphene oxide (rGO) derivatives doped with heteroatoms (N, S) were synthesized and tested for the degradation of acetaminophen by EF process [1,2].

Experimental

Nitrogen (N) and nitrogen/sulphur (N/S) co-doped graphene aerogels were synthesized by hydrothermal method. ORR studies were carried out in order to determine the e^- pathway of the catalyst, $2e^-$ (with H_2O_2 production) or $4e^-$ (direct conversion on H_2O) and EF assays were performed to quantify the degradation rate of ACE with the in situ generation of H_2O_2 by each rGO-doped derivative. Carbon-magnetic catalyst was synthesized to promote the decomposition of H_2O_2 to $HO^{\bullet}$.

Results and discussion

The $2e^-$ ORR process (involving in situ H_2O_2 generation) was mainly obtained using N-doped graphene aerogels and it was related to the content of N functionalities as well as to the porous texture of the samples. The highest pollutant removal (71.0%) and mineralization (51.6%) were obtained with N-doped materials and carbon-Fe_3O_4 catalyst, showing good stability and low iron leaching (0.33 mg L^{-1}).

Conclusions

N/S-doped graphene aerogels show better performance for ORR leading a four- electron pathway and also high current densities**.**

Heterogeneous electro-Fenton process for the degradation of acetaminophen using both N-graphene aerogels and magnetically recoverable catalyst based on carbon-magnetite, allowed a contaminant removal of ca. 100%.

Acknowledgements

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P80

Phenol adsorption-desorption on lignin-derived carbon fibers

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Introduction

Activated carbons have been widely used for the removal of phenol in liquid phase. However, efficient phenol desorption processes are currently being researched. For this reason, the use of lignin-derived carbon fibers, prepared through electrospinning method, as phenol adsorbents from aqueous solutions is presented in this communication.

Experimental

Carbon fibers have been prepared by electrospinning of lignin/ethanol or H_3PO_4/lignin/ethanol solutions [1]. Equilibrium and kinetics adsorption experiments have been carried out in a batch system and adsorption-desorption dynamics experiments have been studied in an adsorption column as well. A mathematical model, developed by our research group, has been used to predict the breakthrough profiles [2].

Results and discussion

Microporous carbon fibers have been obtained by carbonization of electrospun lignin fibers. The incorporation of H_3PO_4 produces carbon fibers with wider microporosity that favors the kinetic adsorption of phenol. The influence of the adsorption temperature has been analyzed, being the adsorption an exothermic process. The regeneration of the saturated carbon fibers has been studied, finding a higher regeneration capacity (70 %) for the P-containing carbon fibers. The use of thermodynamic and kinetic data obtained from batch experiments were properly used in the mathematical model for the prediction of breakthrough profiles.

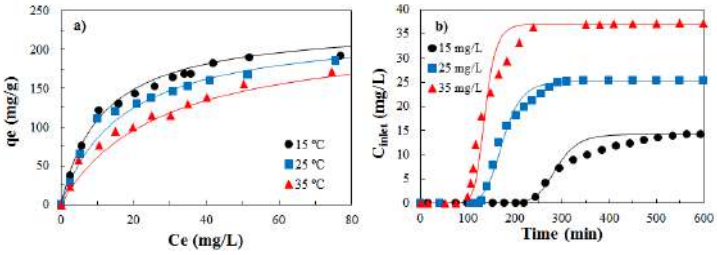

Figure 1. a) Phenol adsorption isotherms at different temperatures and b) breakthrough curves at different inlet concentrations (w: 200 mg, Q: 5 mL/min) on P-containing carbon fibers.

Conclusions

Carbon fibers have been accurately used as adsorbent for phenol removal. The addition of H_3PO_4 to the initial lignin solutions produces carbon fibers with wider porosity, which make faster the phenol adsorption and improve the regeneration of those adsorbents.

Acknowledgements

The authors acknowledge the support by MINECO/FEDER (CTQ2015-68654-R) and MICINN (RTI2018-097555-B-100)

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P81

Promoting Microbial Metabolism on Carbon Materials for Cleaning Wastewaters

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Introduction

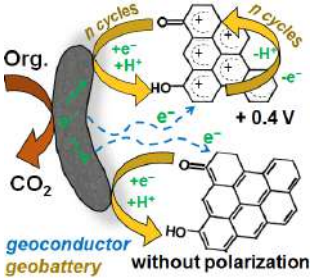
The use of conductive carbon materials to speed up the biodegradation rate in anaerobic biofilters constitutes an attractive emerging field for wastewater treatment. However, the potential capability of these materials and their properties to design efficient systems is still in their infancy. This work analyzes the role of various carbon materials with different properties (graphite, coke, biochar) on promoting microbial extracellular electron transfer, and their potential utilization as electroactive biofilters to clean-up urban wastewaters. Special attention is paid on the performance-determining electrode properties and the mechanisms involved on e-transfer.

Experimental

The physicochemical properties of the materials were characterized by SEM, Raman, XRD, gas adsorption, TPD, XPS and conductivity measurements. The e-transfer capability was studied by CV and chronoamperometry. Biodegradation performance was evaluated from COD removal under different operating conditions by using laboratory-scale up-flow biofilters without and with polarization. Siliceous gravel was used as non-electroconductive control biofilter.

Results and discussion

Results reveal that the electroconductive biochar is the most efficient biofilter material [1]. This is mainly assigned to its large number of electroactive oxygen functionalities, which govern e-transfer through the geobattery mechanism (see the scheme); whereas the electroconductivity, much higher in fossil-derived materials, determine the current production through the geoconductor mechanism (see the scheme). We propose the modulation of quinone-like e-acceptors by anodic polarization to promote the biodegradation capability of carbon materials.



Scheme of the proposed geoconductor and geobattery e-transfer mechanisms between bacteria and carbon materials.

Conclusions

The higher biodegradation efficiency showed by the electroconductive biochar and its associated sustainability will expand the applicability of METs to biofilter-based systems.

Acknowledgements

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